NO_x Control Options and Integration for US Coal Fired Boilers

Quarterly Progress Report

Reporting Period Start Date July 1, 2003
Reporting Period End Date: September 30, 2003

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October 31, 2003

DOE Cooperative Agreement No: DE-FC26-00NT40753

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Abstract

This is the thirteenth Quarterly Technical Report for DOE Cooperative Agreement No: DE-FC26-00NT40753. The goal of the project is to develop cost effective analysis tools and techniques for demonstrating and evaluating low NO_x control strategies and their possible impact on boiler performance for boilers firing US coals. The Electric Power Research Institute (EPRI) is providing co-funding for this program. This program contains multiple tasks and good progress is being made on all fronts.

The corrosion probe task is proceeding: Two plant visits were made to prepare for field testing and shakedown tests for the probes were conducted at the University of Utah's L1500 furnace. Corrosion probes will be installed at the Gavin Plant site in the next quarter. Laboratory studies of SCR catalyst continued this quarter. FTIR studies of catalyst sulfation and of adsorption of NH3 and NO were continued at BYU. NO activities have been measured for a number of samples of BYU catalyst and insights have been gained from the results. Plans are being detailed to test monolith and plate catalysts exposed in the field. In this quarter, the catalysts in the slipstream reactor at AEP's Rockport plant were exposed to the dusty flue gas for 1695 hours. Thus the cumulative catalyst exposure to flue gas rose from 980 hours last quarter to 2677 hours in this quarter. Loss of catalyst activity was noted between April (when the catalysts were fresh) and August. Further analysis of activity data will be needed.

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Executive Summary

The work to be conducted in this project received funding from the Department of Energy under Cooperative Agreement No: DE-FC26-00NT40753. This project has a period of performance that started February 14, 2000 and continues through December 30, 2004.

Our program contains five major technical tasks:

- evaluation of Rich Reagent Injection (RRI) for in-furnace NO_x control
- demonstration of RRI technologies in full-scale field tests at utility boiler
- impacts of combustion modifications (including corrosion and soot)
- ammonia adsorption / removal from fly ash
- SCR catalyst testing

To date, good progress is being made on the overall program. We have seen considerable interest from industry in the program due to our successful initial field tests of the RRI technology and the corrosion monitor.

During the last three months, our accomplishments include the following:

- Monthly project meetings have been held on the corrosion probe task. Two plant visits were made to prepare for field testing, and shakedown tests for the probes were conducted at the University of Utah's L1500 furnace. Corrosion probes will be installed at the Gavin Plant site in the next quarter.

- The outlet of the BYU FTIR reactor was discovered to be plugged with catalyst powder that impeded gas flow. Consequently, two more sulfation tests with unobstructed outlets were made to verify that the surface vanadia content would be reasonable and consistent with previous results.

- NH_3 and NO adsorption behaviors, individually and in combination, were investigated at BYU by both FTIR and MS analysis of three samples: wet sulfated, dry sulfated, and fresh 5% V_2O_5/TiO_2. XPS analysis was performed to determine surface element atom % of each sample.

- Tests in the CCS examined how consistent the reactors are in their conversion with the same amount of the same catalyst (BYU). Efforts to calibrate mass flow controllers have improved the consistency of reactor concentrations. Conversion data have been computed for the BYU catalyst and insights have been gained from the results.

- Plans are being detailed to test monolith and plate catalysts exposed in the field. The catalysts will be cut such that a lengthwise piece is saved for future tests, while the remainder is cut up into smaller segments, each of which will be tested and characterized individually to form a picture of the poisoning/activity profile along the length of the catalyst.

- Catalysts in the slipstream reactor at AEP's Rockport plant were exposed to the dusty flue gas for 1695 hours. Thus the cumulative catalyst exposure to flue gas rose from 980

hours last quarter to 2677 hours in this quarter. Loss of catalyst activity was noted between April (when the catalysts were fresh) and August.

- The Rockport plant is currently in an outage that will last until November. The slipstream reactor is not operating during the outage.

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Experimental Methods

Within this section we present in order, brief discussions on the different tasks that are contained within this program. For simplicity, the discussion items are presented in the order of the tasks as outlined in our original proposal.

Task 1 - Program Management

During the last performance period,

- Corrosion Probe:
  - Plant visits were made to Gavin to prepare for field tests and to discuss with plant personnel, tasks to complete before arrival of equipment.
  - Installation of equipment and start of field testing is planned for next performance period.
- SCR:
  - BYU continued both the *in situ* FTIR studies and catalyst activity testing.
  - Slipstream reactor at Rockport has accumulated a total of 2677 hours of testing.
  - Plant visit to Rockport was made to remove catalyst and provide it to BYU for analysis.
  - Coordinated visit was made to coincide with Hg sampling tests for a second project that is using the SCR reactor
  - Testing stopped on Rockport Unit 1 due to a plant outage. Outage will continue into next performance period.

Industry Involvement

Results from portions of this research program have been reported to industry through technical presentations at recent conferences:

- Two papers and a poster will be presented at the DOE NETL Conference on SCR and SNCR for Control of NO_x to be held October 29-30, 2003 in Pittsburgh, PA:
  - Marc Cremer, David Wang, E. Schindler, “Improved Rich Reagent Injection (RRI) Performance For NO_x Control In Two Coal Fired Utility Boilers.”
  - Constance Senior, Temi Linjewile, Michael Bockelie, Eric Eddings, Kevin Whitty, Larry Baxter, “SCR Deactivation Mechanisms Related to Alkali and Alkaline Earth Elements.”
  - Dave Swensen and Darren Shino, “Control Systems for Long-Term Field-Testing Applications.” (poster)
- Two papers were accepted for presentation at the Electric Power Conference 2004 to be held March 31- April 1, 2004 in Baltimore, MD:
  - Mark Cremer, Davud Wang, and Bradley Adams, "Design of Reagent Injection Systems for NO_x Control In Coal Fired Utility Boilers.”
  - Constance Senior and Temi Linjewile, “Understanding Oxidation of Mercury Across SCR Catalysts in Power Plants Burning Low Rank Coals.”

Task 3 - Combustion Impacts

The existing corrosion system was configured for a single corrosion probe. In order to build a multi-probe system, additional probes have been fabricated, noise modules and all electronics have been purchased and the data collection software (LabView) has been modified to accept inputs from multiple probes. Existing software and electronics have been modified to add the ability to collect, process and store input signals from sensor elements in six corrosion probes. A description of the work performed is given below.

Probe Design Modifications Improvements and Assembly

The design of the probe has been modified to accommodate a 2-inch probe instead of the 3-inch probe used in the first program. This will aid in cooling and will require at most two high-pressure boiler tubes to be bent for each penetration that is required to insert a probe. Another improvement to the probe has been in the use of "quick disconnects" for the electronics and tubing. This makes it much easier to attach the probe to the data collection boxes.

Heat transfer analyses of the modified probe design have been completed. In these analyses, it was estimated that nearly 5000 SCFH of air are needed to cool a single probe. In addition, the back end of each of the probe sensor elements has deep serrations that will facilitate cooling. Drawings of the probe were completed and submitted to a machine shop for fabrication. In summary, the modified design focuses on ensuring that there is adequate cooling for the probes and that choked flow conditions are not encountered. Further, fewer sensor plates are used in the sensor element assembly, making it necessary to pay particular attention to the mounting of the thermocouples. The thermocouple sheaths are shielded from the sensor reference plate to prevent a short between the sensor signal and the probe body.

All planned probe design modifications have been implemented. A single probe was assembled and prepared for shakedown tests. A central control box was also assembled for preliminary testing.

Ordering of Long Lead-Time Items

The long lead-time items such as the ceramic plates for the sensor elements, and the SMC electro-pneumatic regulator valves for probe cooling air control have been ordered. Other items including electrical connectors and thermocouples with their connectors have also been ordered and received.

Software Modification and Data Acquisition Equipment

The existing software and electronics were modified to add the ability to collect, process and store input signals from sensor elements in six corrosion probes. The software modification can be broken down into Fieldpoint Real Time (RT) Applications and Host Applications. The Fieldpoint RT Applications perform the following functions:

- Read thermocouple data
- Read noise module voltage data
- Read noise module current data
- Log data to flash memory
- Make calculations for electrochemical noise corrosion rate (mm/yr) and ERN
- Publish data to host PC

The Host Applications perform the following functions:

- Read data from RT applications (ENCR, ZRA, ECN, EPN, ERN, three temperatures)
- Act as VI-server control for each probe's temperature set point
- Provide manual operation of control valves, temperature control and air shutoff valve
- Prepare probe signal comparison charts
- Log Data

A new improvement in the electronic hardware being pursued is the use of wireless communication links between the probe control boxes and the host computer. During this reporting period, an engineer from REI visited the Gavin plant to assess the feasibility of using wireless communication hardware.

Other hardware for data acquisition and control including power supplies, breakers, cable connectors, Ethernet switches and fiber-optic media converters have been ordered and received.

Communication between the probes and the host computer

The proposed configuration of the probe boxes is shown in Figure 1. The network of probes consists of a central control box that receives and sends signals to all the probes but also serves as the control box for the central probe on the south boiler wall. All the probes on the south boiler wall are connected to the central box via Ethernet cables. The central control box communicates with the host site PC via a fiber optic cable. The single probe on the north boiler wall is connected to the central control box via a fiber optic cable and is also provided with a wireless communication capability.

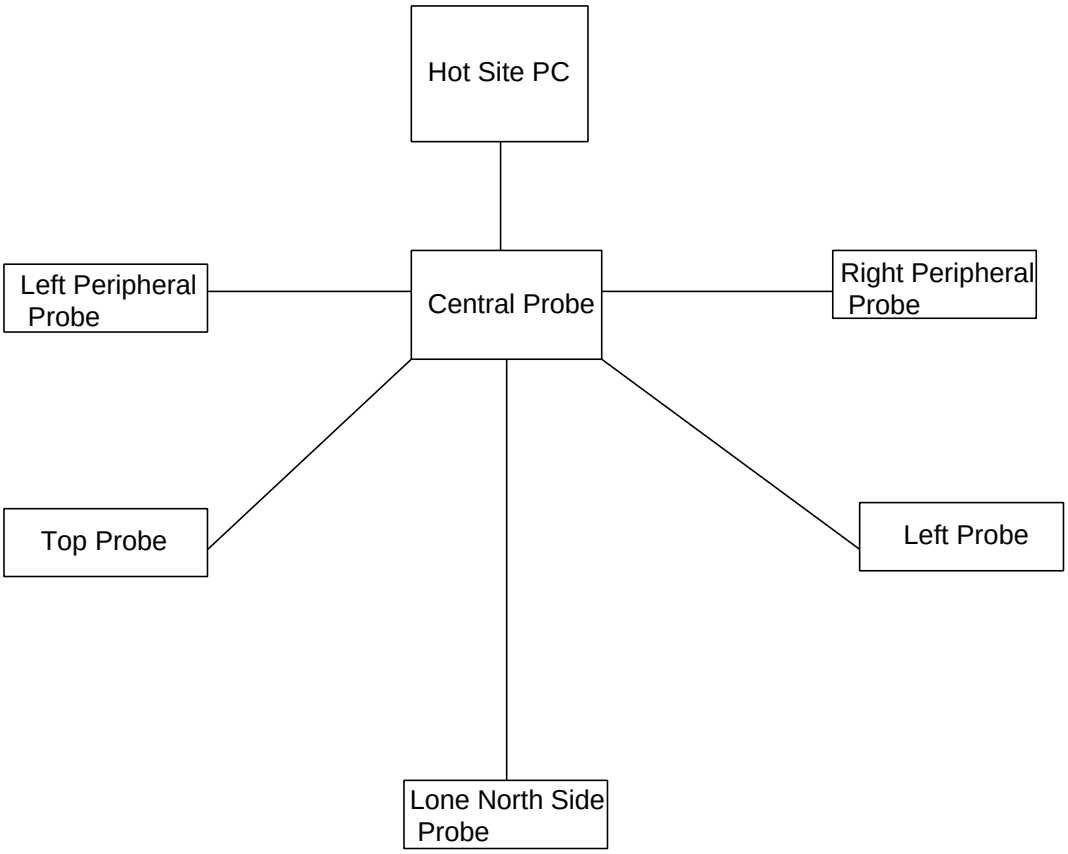

Figure 1. Configuration of the network of probes.

Probe Shakedown Tests

The focus of activity in the reporting period was to conduct shakedown tests for the probes. The objective of the shakedown tests was to identify and rectify problems that might arise during operation of the modified corrosion monitoring system before shipping to the field test site. A description of the work conducted during the shakedown tests is presented below.

Furnace Preparations

Before shakedown tests could begin, the L1500 furnace had to be started and heated to operating temperature. This is a gradual process that takes about one week. The furnace was started on Friday, August 29, 2003 and was ready for testing on Tuesday, September 2, 2003. However, the probe was not inserted into the furnace until Friday, September 5, 2003 due to delays in having the probe and electronics ready. The following is a summary of the activities that transpired to make the probe ready for testing.

Probe Preparations

A cooling air intake was welded to the probe. The air intake fixture is a threaded pipe nipple, which allows a Chicago style fitting to be connected to the probe. Welding the fixture resulted in warping of the probe body and made it impossible to insert the internal parts. To correct this problem, the probe was taken to a machine shop where the warping was corrected by shaving off metal in the probe's interior around the air intake fixture. Figure 2 shows the face of a fully assembled probe. The next step was to obtain two air hoses fitted with Chicago fittings. One hose

connected air from the compressed air wall outlet to the control valve and a second hose connected the outlet of the control valve to the probe body. Air hoses capable of an operating pressure of 150 psi were selected.

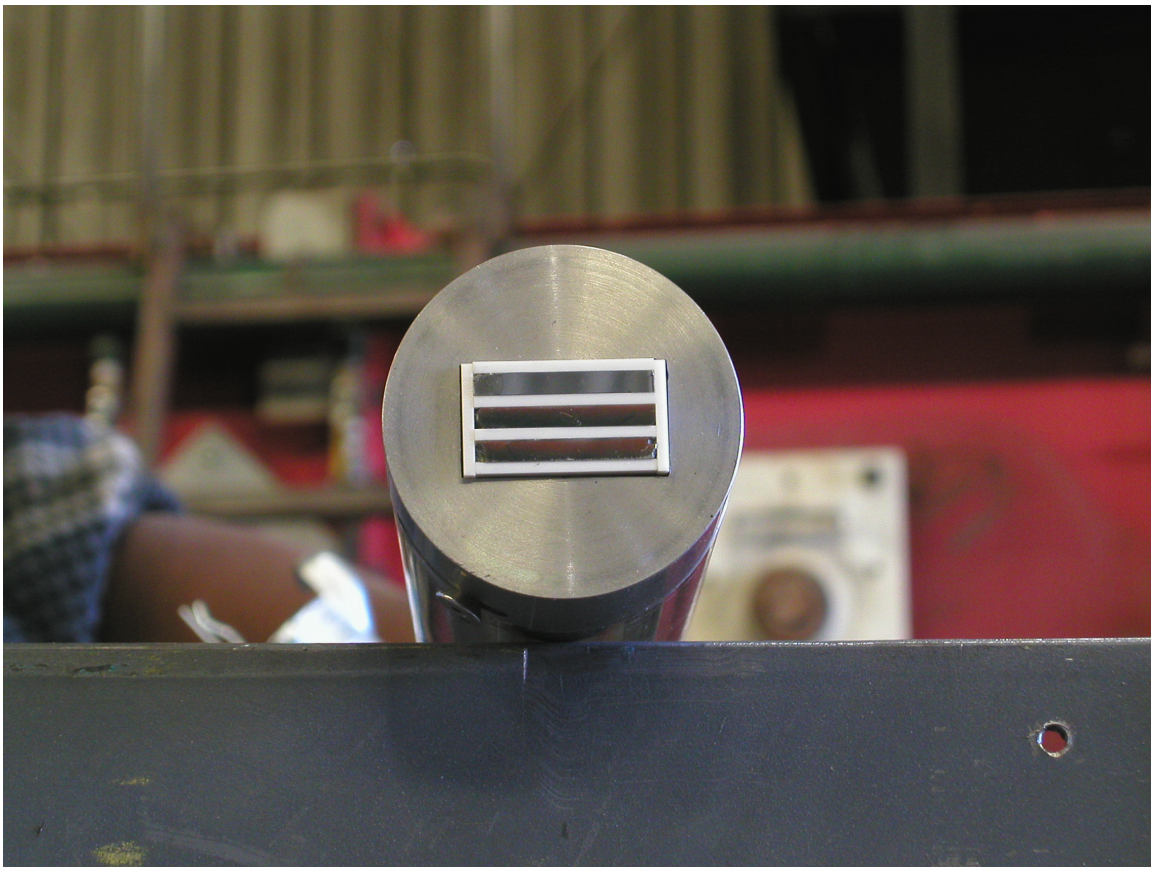

Figure 2. Corrosion sensor plates mounted into the probe body.

Host Computer

A host desktop computer was set up for data acquisition and control of the probe. Installation involved setting up LabView software and IP addresses for web-based communications. Initial tests involved establishing communication between the PC and the central control box.

Control Boxes

For the plant tests at Gavin, there will be six control boxes: a central control box (24”x24”x8”) and five smaller (16”x16”x8”) satellite boxes connected to the central box. The central box will be connected to the five probes located on the south wall by Ethernet cables. The single probe located on the north wall will be connected to the central box via a fiber optic cable and wireless communication. Figure 3 shows a picture of the control box for the probe to be mounted on the north wall. The central box is connected to the Host PC via a fiber optic cable. The central control box has been assembled and was tested during the shakedown tests at the L1500 furnace.

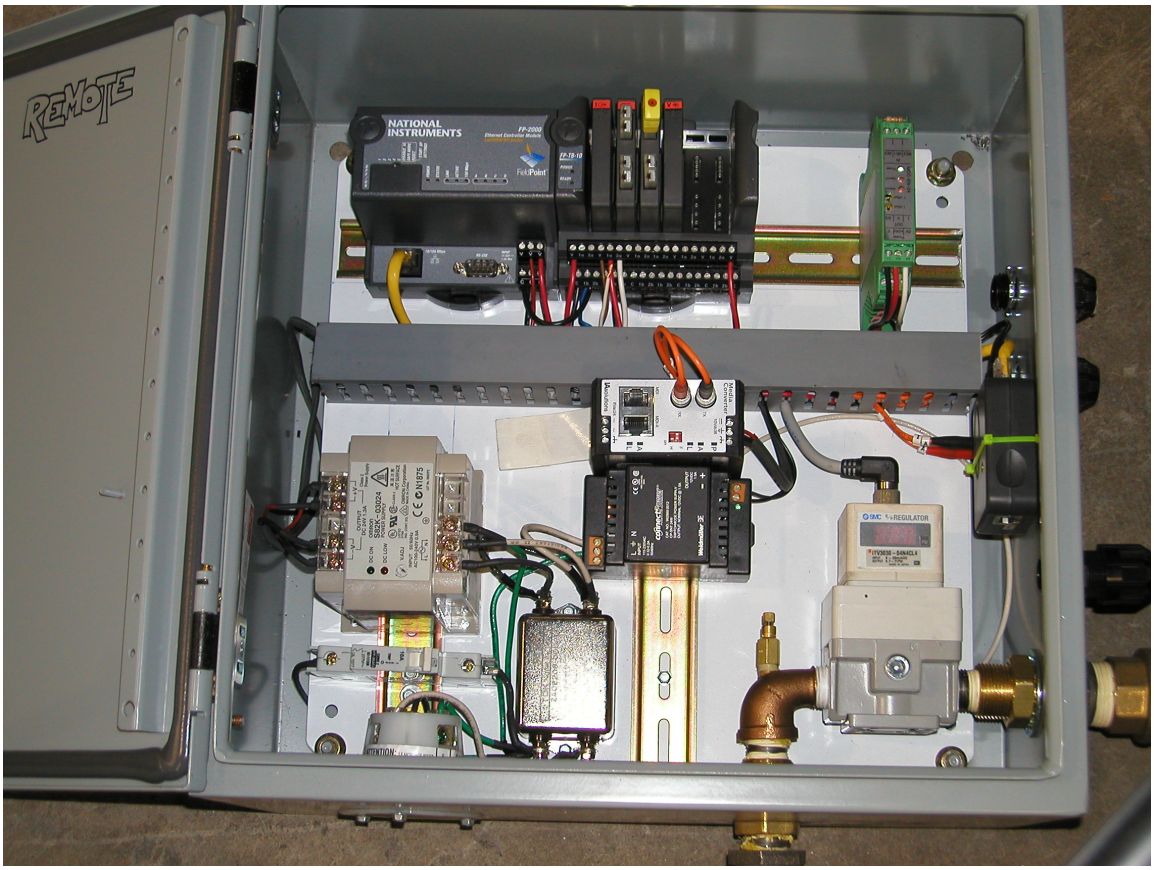

Figure 3. Control box for the single probe on the north wall.

Shakedown Test Runs

Testing of the new probe in the L1500 commenced on Tuesday, September 2, 2003 and ended on Friday, September 12, 2003. The probe was gradually inserted into a furnace port and locked into position using a flange specially fabricated for this test. During the probe insertion stage, the air control valve was opened fully. The sensor temperature did not rise much. To observe a significant temperature rise, the air control valve had to be shut almost completely. This was due to the low furnace temperature and heat fluxes, which were later adjusted. Once the probe temperature response was established, the sensor was advanced further into the furnace port. When the sensor temperature reached the 400 – 550°F window, a response in the current signal was observed. The probe temperature was allowed to rise to about 750°F and in some cases to 840°F. In response, the current signal increased with an increase in sensor temperature. It may be noted, however, that potential signal stayed at zero all the time and the FP module showed "out of range." This problem was later found to be due to software configuration of the FP modules. Once this was rectified, both the current and potential signals responded appropriately. In addition, more troubleshooting had to be done to resolve the temperature control system, especially the mapping between the valve opening, the air pressure, and the 4-20 mA signal.

Figure 4 shows probe response as a function of time at a specified sensor temperature. It may be noted that the test results showed the expected trends and magnitudes in corrosion rates as a function of sensor temperature.

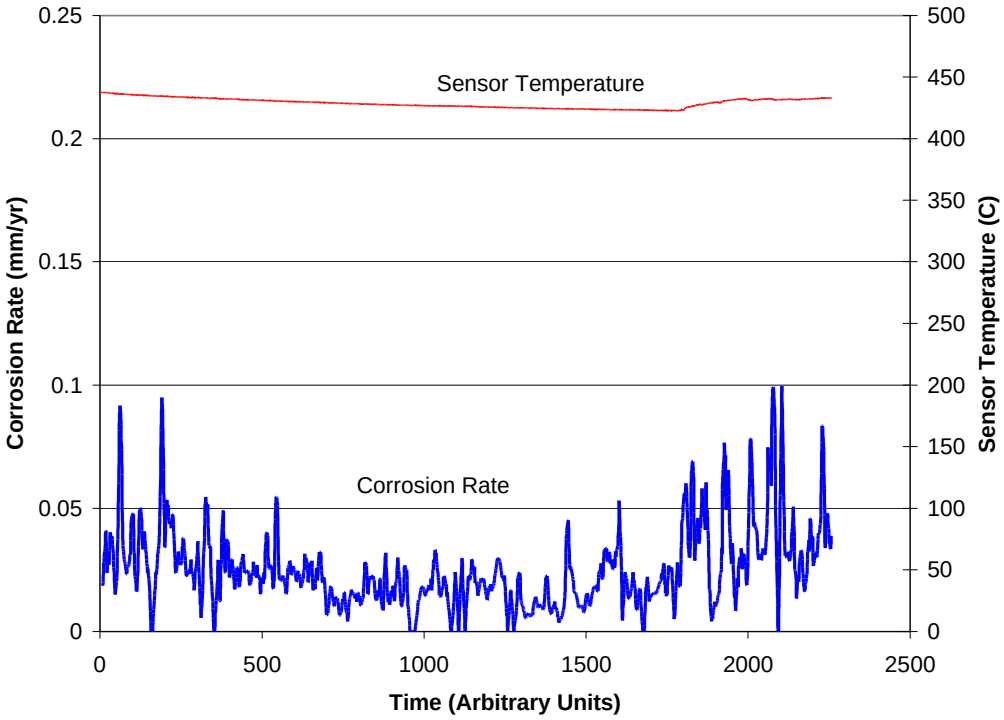

Figure 4. Response of the modified corrosion sensor in a furnace maintained at 2105°F.

During shakedown tests, several problems arose and were resolved. These included:

- Warping of the probe air intake fixture during welding
- Failure of the control valve to shutoff completely when the control input signal was 4mA
- Leakage of air through the sensor plates
- Air leakage at a fitting on the outlet of the control box
- Faulty wiring of thermocouple connector pins produced an error on the Field Point modules
- Problems with temperature control software
- Problems with the EN measurement and correct calculation of corrosion rates
- Improper configuration of the S-One noise modules in the software and hardware caused an “out of range” error message

Task 4 - SCR Catalyst Performance under Biomass Co-Firing

The cost and effectiveness of NO_x control strategies for coal-fired boilers have received considerable attention over the last two decades and a number of successful approaches have been applied. Utilities weigh a number of issues when determining the best strategy for their specific units. Comparisons routinely include cost and the amount of NOx reduction, with selective catalytic reduction (SCR) often used as a standard for comparison. However, to make this comparison meaningful, the total cost of combustion modifications must be considered (carbon-in ash levels, waterwall wastage, etc.). Industry is developing experience evaluating many of these costs and it is one of the tasks of this program to better understand two such areas – waterwall corrosion and soot formation. For SCR, the "real" cost for coal-fired boilers using US coals and coal/biomass blends is uncertain.

The economics of SCR are closely tied to catalyst costs, including initial investment cost and the cost of regeneration or replacement. The need for data and models that enable assessment of such costs is emphasized.

The purpose of this task is to develop databases and a model for assessing catalyst deactivation and its effects on SCR catalyst life and cost. Within this task there are four principal subtasks:

1. technology assessment and fundamental analysis of chemical poisoning of SCR catalysts by alkali and alkaline earth materials;
2. evaluation of commercial catalysts in a continuous flow system that simulates commercial operation;
3. evaluation of the effectiveness of catalyst regeneration; and
4. development of a model of deactivation of SCR catalysts suitable for use in a CFD code.

Subtasks 1 and 3 are principally performed at Brigham Young University (BYU) under the direction of Profs. Larry Baxter, Calvin Bartholomew, and William Hecker. The work effort for Subtasks 2 and 4 is being performed by REI, with assistance from the University of Utah and BYU. Progress during the last performance period on Subtasks 1 and 2 is described below.

Task 4.1 Technology Assessment/Fundamental Analysis

The objectives of this subtask are (1) to supplement the SCR-catalyst-deactivation literature with results from new laboratory-scale, experimental investigations conducted under well-controlled and commercially relevant conditions in the presence of SO_2, and (2) to provide a laboratory-based catalyst test reactor useful for characterization and analysis of SCR deactivation suitable for samples from commercial facilities, slipstream reactors, and laboratory experiments. Two catalyst flow reactors and several additional characterization systems provide the analytical tools required to achieve these objectives. The flow reactors include the *in situ* surface spectroscopy reactor (ISSR) and the catalyst characterization system (CCS), both of which are described in more detail in previous reports. Additional characterization systems include a temperature-programmable surface area and pore size distribution analyzer, scanning electron microscopes and microprobes.

The sample test matrix includes two classes of catalysts: commercial, vendor-supplied SCR catalysts and research catalysts synthesized at BYU. The commercial catalysts provide immediate relevance to practical application while the research catalysts provide unfettered ability to publish details of catalyst properties. The five commercial catalysts selected for use come from the most commercially significant catalyst manufacturers and provide a wide range of

catalyst designs and compositions. The in-house catalysts will be subjected to detailed analysis, activity testing, and characterization, thus providing a comprehensive test and analysis platform from which to determine rates and mechanisms of catalyst deactivation. The result of this task will be a mathematical model capable of describing rates and mechanisms of deactivation. Within the last performance period, *in situ*, spectroscopic experiments partially reported last quarter were completed. The most significant finding of these investigations is a consistent indication that vanadium does not sulfate during SCR activity in the presence of gas-phase SO_2 while both the substrate (anatase) and modifiers (molybdenum) do. In addition, mass-spectroscopy-based analyses of product gases from this reactor system help elucidate fundamental kinetics and deactivation mechanisms.

ISSR Overview

The purpose of the FTIR-ISSR is to provide definitive indication of surface-active species through *in situ* monitoring of infrared spectra from catalytic surfaces exposed to a variety of laboratory and field conditions. The ISSR provides *in situ* transmission FTIR spectra of SO_2, NH_3, and NO_x, among other species. Absorption and desorption behaviors of these and other species are monitored. Quantitative indications of critical parameters, including Brønsted and Lewis acidities on fresh and exposed catalysts, are included. Indications of coadsorption of NH_3 and NO_x help elucidate mechanisms and rates of both reactions and deactivation.

FTIR transient test reactor

Experimental conditions for the most recent vanadium sulfation experiments appear in Table 1. The sample designated VTOB serves as a control in this matrix, being preoxidized but not sulfated.

In situ IR spectra collected for VTHB and VTOC following sulfation are shown in Figure 5 and Figure 6. Figure 5 and Figure 6 show that sulfate bands are smaller following wet sulfation compared to the sulfate peak collected when the IR reactor cell was partially plugged (Figure 7 and Figure 8). In addition, the sulfate peak position stays almost unchanged (around 1370 cm^{-1}) during the sulfation process, while it shifted to a higher wave number when the cell outlet was obstructed.

Table 1. Sulfation test conditions.

Sample Name	Sample Details	Notes	Gas Stream Composition, %				Flow (sccm)	Temp (°C)
			He	O_2	SO_2	H_2O		
VTHB	5% V_2O_5/TiO_2	Preoxidation	89.4	10.6		0	50	380
		24 Hours Sulfation	93.6	6.2	0.17	2.4	63.3	380
VTOB	5% V_2O_5/TiO_2	Preoxidation	91.9	8.1		0	48.5	380
VTOC	5% V_2O_5/TiO_2	Preoxidation	91.9	8.1		0	48.5	380
		24 Hours Sulfation	93.5	6.3	0.17	0	62.1	380
VTHC	5% V_2O_5/TiO_2	Preoxidation	91.9	8.1		0	48.5	380
		24 Hours Sulfation	93.6	6.2	0.17	2.4	63.3	380
VTHD	5% V_2O_5/TiO_2	Preoxidation	91.9	8.1		0	48.5	380
		24 Hours Sulfation	93.6	6.2	0.17	2.4	63.3	380

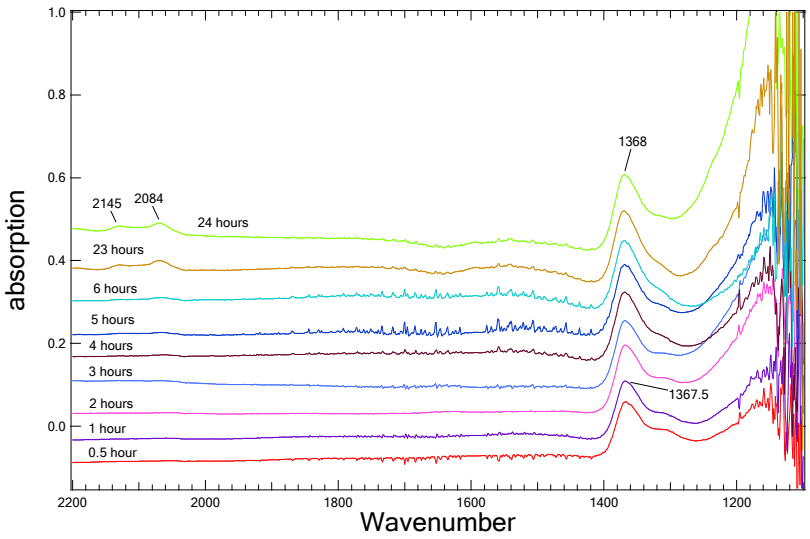

Figure 5. *In situ* IR spectra of 5% V_2O_5/TiO_2 during wet sulfation (VTHB).

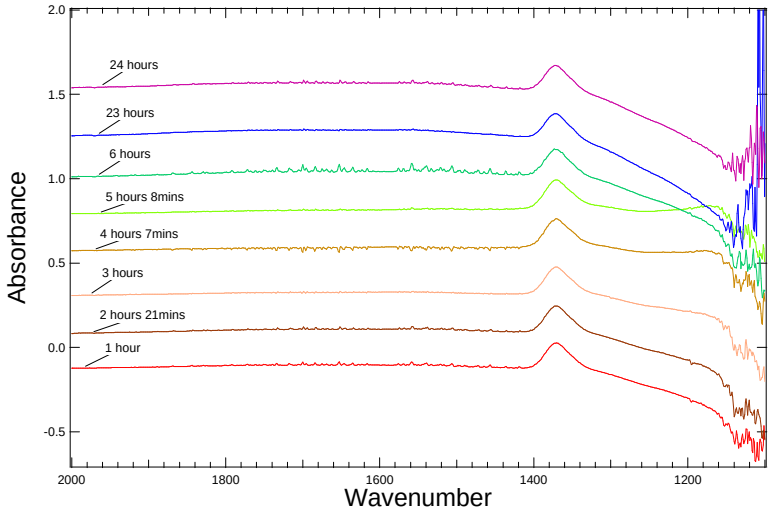

Figure 6. *In situ* IR spectra of 5% V_2O_5/TiO_2 during dry sulfation (VTOC).

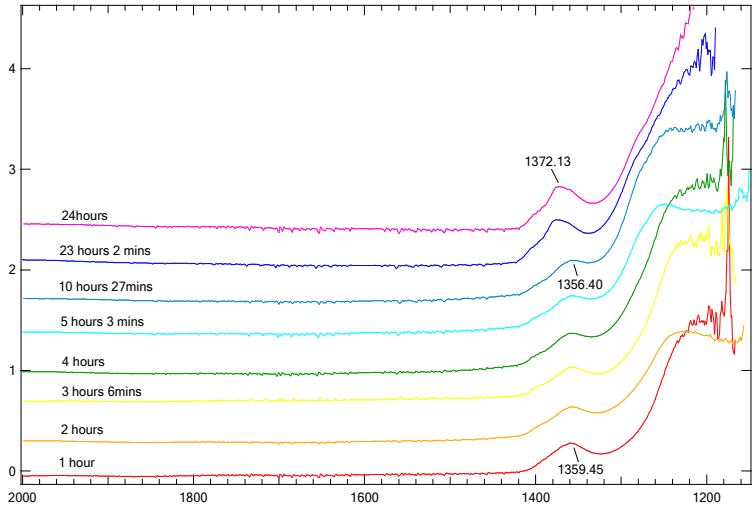

Figure 7. *In situ* IR spectra of 5% V_2O_5/TiO_2 during wet sulfation (VTHA) when IR reactor cell was plugged.

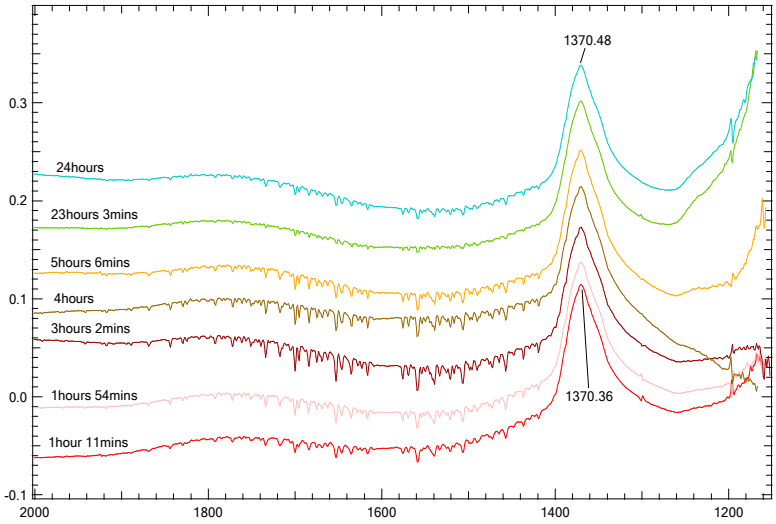

Figure 8. *In situ* IR spectra of 5% V_2O_5/TiO_2 during dry sulfation (VTOA) when IR reactor cell was plugged.

NH_3 and NO introduced both individually and in combination after surface sulfation of the three catalysts types – VTHB (wet sulfated), VTOB (dry sulfated), and VTOC (non-sulfated) – indicate how reactions affect sulfation. NH_3 adsorption behavior results at room temperature, 100°C, 200°C, 300°C, and 380°C on all three samples (VTHB, VTOC, and VTOB) appear in Figure 9 through Figure 14.

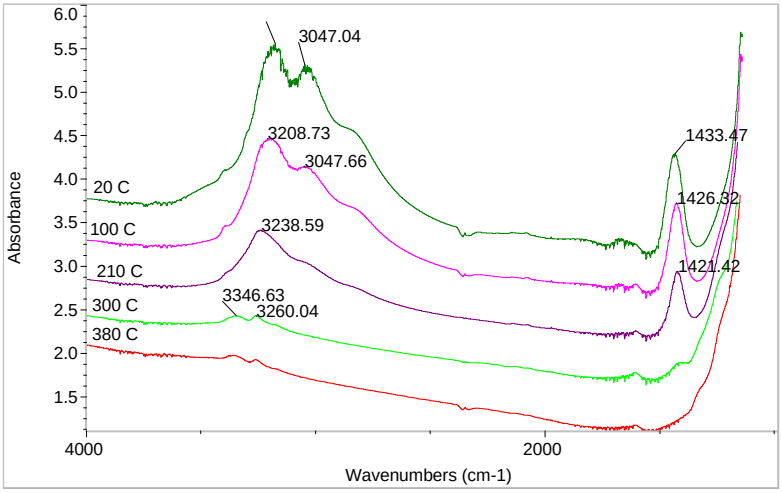

Figure 9. NH_3 adsorption on VTHB at different temperatures.

Following ammonia adsorption on pre-sulfated samples, three new bands appear relative to IR spectra collected during sulfation: one at 1433 cm^{-1}, and two overlapping bands between 2900 to 3350 cm^{-1}. The IR absorption band at 1433 cm^{-1} indicates a bending vibration of ammonia chemisorbed on Brønsted acid sites on the sulfated catalyst surface. No absorption was observed at 1640 cm^{-1}, a peak that reportedly corresponds to the vibration of ammonia chemisorbed on Lewis acid sites. The absorption bands observed at 2900-3350 cm^{-1} represent stretching vibration of ammonia adsorbed on both Brønsted (~ 3030 cm^{-1}) and Lewis acid (~3350 cm^{-1}) sites on the

catalyst surface. These results indicate that ammonia adsorbs mainly on Brønsted acid sites on the sulfated catalyst surface, suggesting that after sulfation the acid sites on the catalyst surface are principally of the Brønsted type.

Some NH_3 remained on the catalyst surface even after the temperature was increased to 200 °C, having desorbed to concentration at or below detections limits at 300 °C.

Figure 10 through Figure 14 compare NH_3 adsorption behavior on different catalyst samples; Samples A, B, and C correspond to wet-sulfated, dry-sulfated, and fresh 5% V_2O_5/TiO_2 catalysts, respectively.

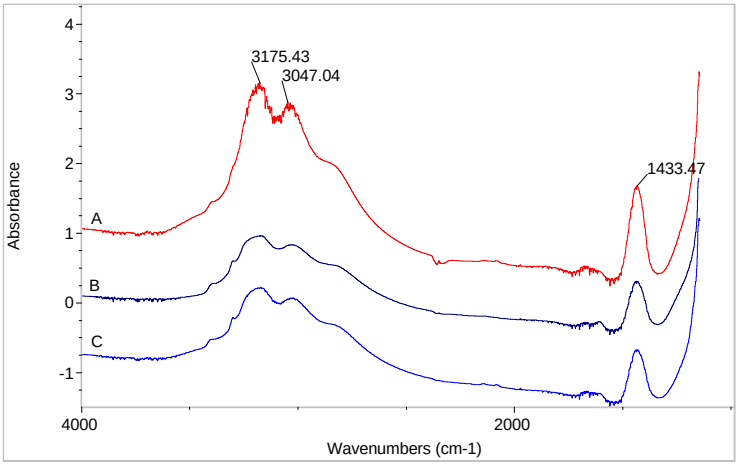

Figure 10. NH_3 adsorption on different samples at room temperature.

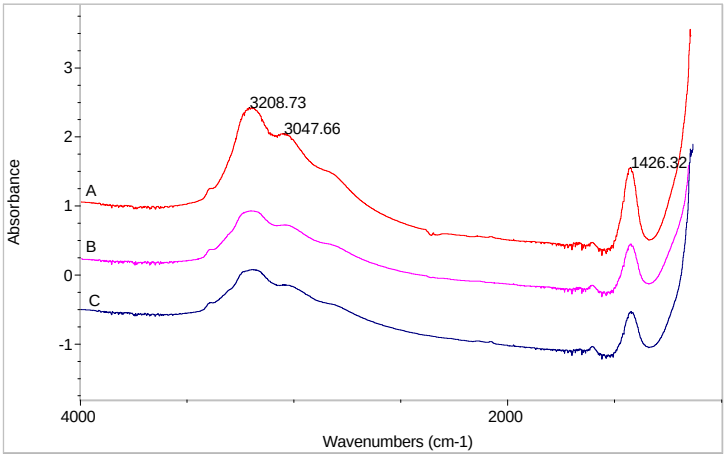

Figure 11. NH_3 adsorption on different samples at 100 °C.

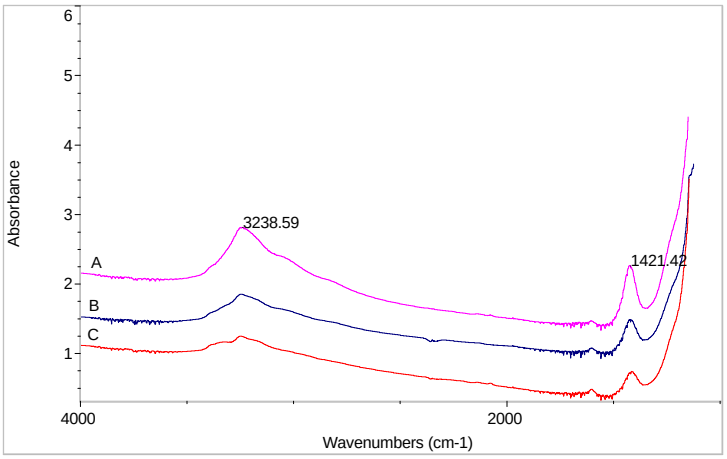

Figure 12. NH_3 adsorption on different samples at 200 °C.

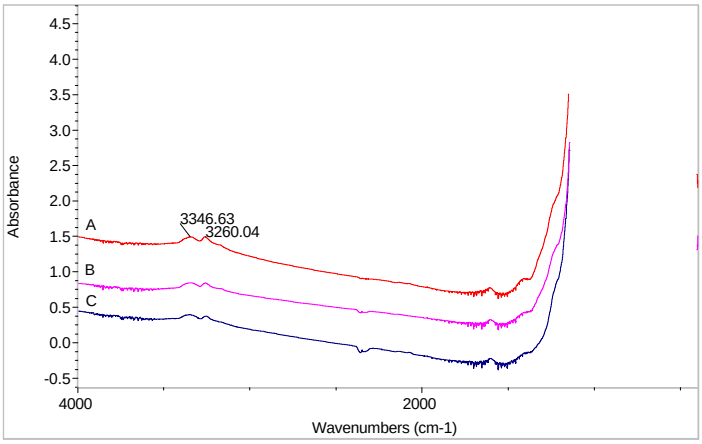

Figure 13. NH_3 adsorption on different samples at 300 °C.

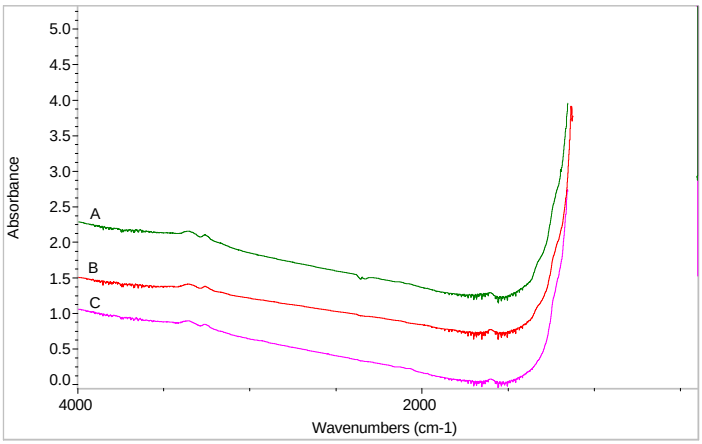

Figure 14. NH_3 adsorption on different samples at 380 °C.

Figure 10 indicates that NH_3 adsorbs on wet sulfated 5% V_2O_5/TiO_2 catalyst (A) more strongly at room temperature as compared to dry sulfated catalyst (B) and fresh 5% vanadia catalyst (C). As temperature increases, NH_3 desorbs from the catalyst surface. Above 100°C and below 200 °C, NH_3 adsorption peaks on wet sulfated 5% V_2O_5/TiO_2 catalyst (A) remain the strongest among the three vanadia catalysts A, B, and C (Figure 11 and Figure 12). At 200°C (Figure 12), the bands for NH_3 adsorption of B (dry sulfated 5% vanadia catalyst) are slightly more intense than those for C (5% fresh vanadia catalyst). When the temperature reaches 300 °C (Figure 13), the NH_3 is nearly desorbed from all three catalyst surfaces. The data indicate that sulfation helps to increase surface acidity, especially Brønsted acidity of vanadia catalyst surfaces. Comparison of NH_3 adsorption on the three different samples at different temperatures indicates a trend of decreasing acidity as follows: wet sulfated vanadia catalyst > dry sulfated vanadia catalyst ≥ fresh vanadia catalyst.

NO adsorption conducted on each of the above three samples after NH_3 adsorption helps determine the extent of surface vs. heterogeneous reaction during SCR. 100 ppm NO introduced to VTHB produced no NO adsorption IR peak (~1619 cm^{-1}), as indicated in Figure 15. However, increasing the NO concentration up to 2% produced a distinct NO adsorption peak (Figure 16). From our observations, NO adsorption usually occurs only at room temperature; accordingly, NO (2%) adsorptions on VTOB and VTOC are reported here only at room temperature, as shown in Figure 17 and Figure 18.

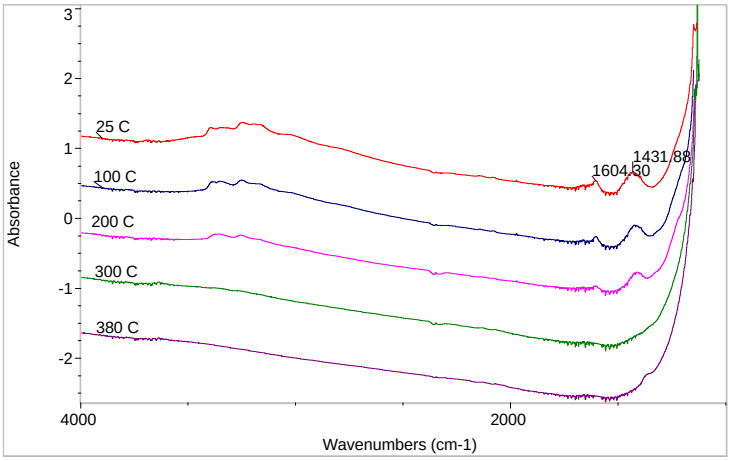

Figure 15. 100 ppm NO adsorption on VTHB at different temperature.

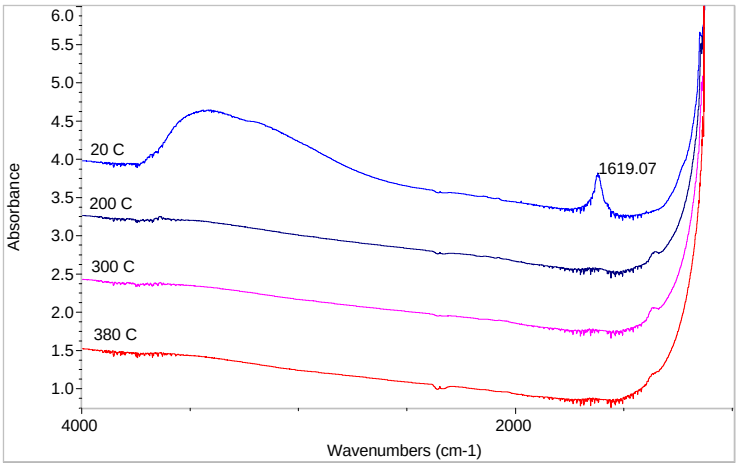

Figure 16. 2% NO adsorption on VTHB.

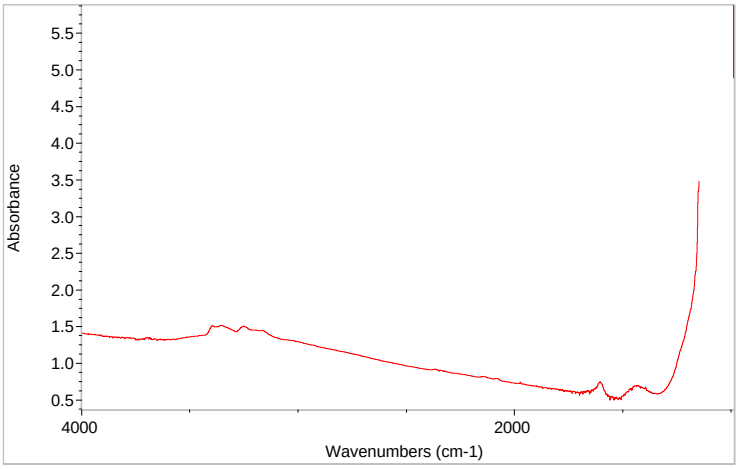

Figure 17. NO adsorption on fresh 5% V_2O_5/TiO_2 at 25 °C.

Figure 18. NO adsorption on dry sulfated 5% V_2O_5/TiO_2 at 25 °C.

NO adsorption was not observed on either the fresh or dry sulfated vanadia catalyst.

These investigations indicate that sulfation has little qualitative impact on species adsorption, although wet sulfation appears to slightly increase ammonia adsorption.

Mass Spectrometry study

NH_3 and NO coadsorption on vanadia catalysts (VTHB, VTOB, and VTOC) was monitored by mass spectrometry (MS) analysis. The original MS results are shown in Figure 19, Figure 20, and Figure 21 in the form of plots of intensity versus time. There are two relatively flat regions in each figure, the first corresponding to the signal for the feed composition and the second corresponding to that for product composition.

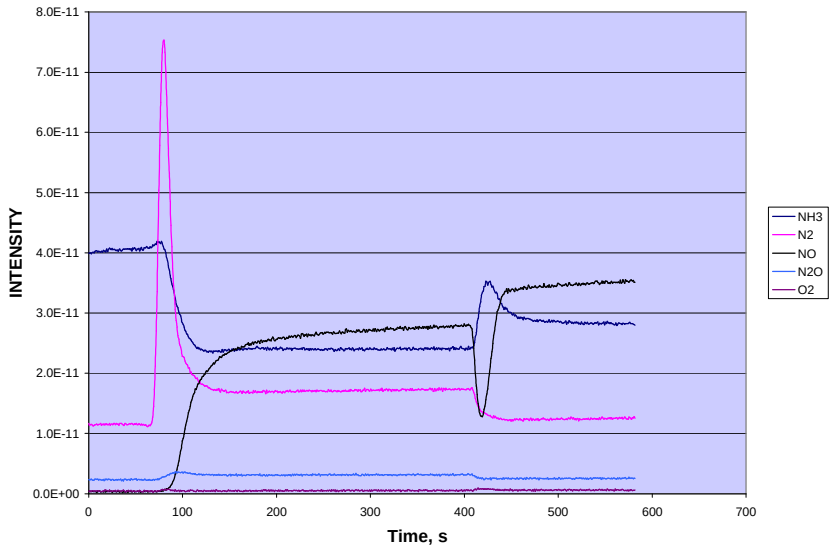

Figure 19. NH_3 & NO coadsorption on dry sulfated vanadia catalyst at 380 °C.

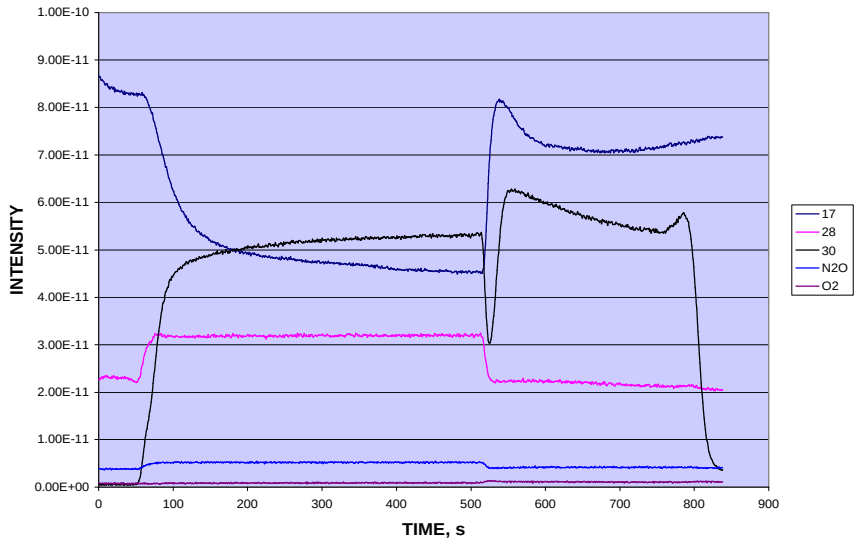

Figure 20. NH_3 & NO coadsorption on fresh vanadia catalyst at 380 °C.

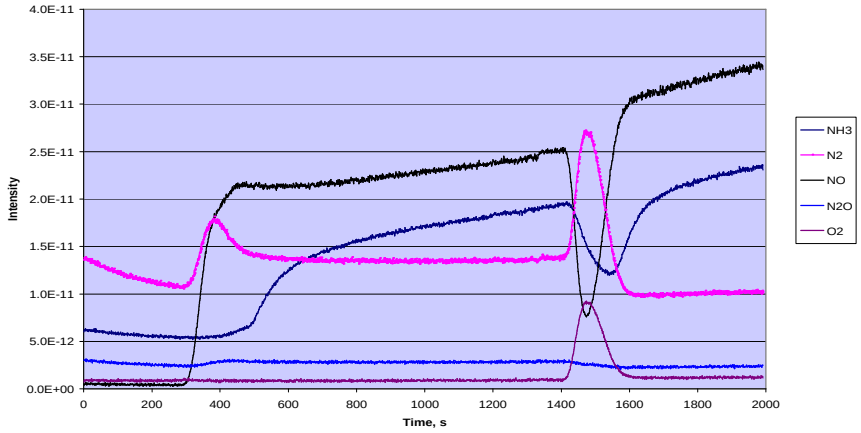

Figure 21. NH_3 & NO coadsorption on wet sulfated vanadia catalyst at 380 °C.

In comparing the N_2 intensity versus time curves for the three samples, an unexpected trend is observed, which is shown in Figure 22 and Figure 23.

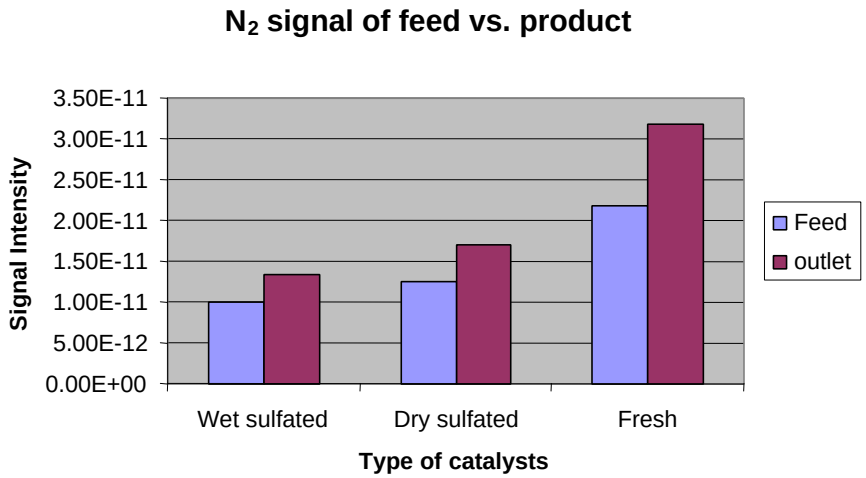

Figure 22. MS results of N_2 signal of feed vs. product.

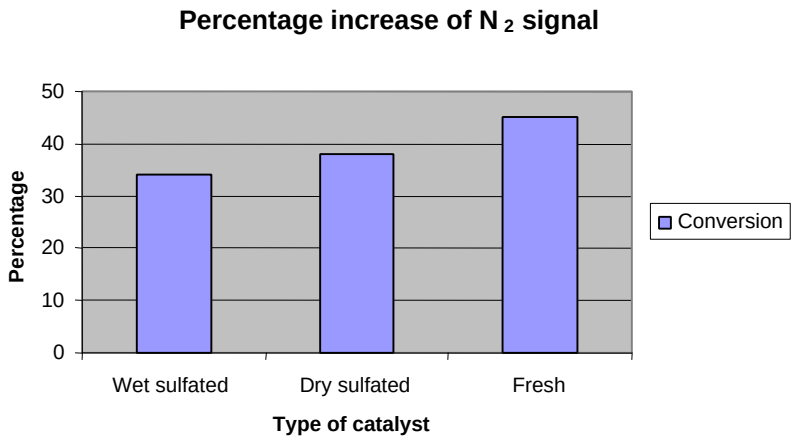

Figure 23. Comparison of percentage increase of N_2 signal.

The increase in N_2 signal intensity following the introduction of NH_3 and NO in helium to the catalyst at 380 °C indicates that the NH_3+NO reaction occurs on the catalyst surface *in the absence of* O_2. NH_3 and NO reaction to produce N_2 at 380 °C in the absence of O_2 appears in some of the literature, consistent with these observations. Moreover, comparison of the percentage increase of N_2 signal shows that unsulfated 5% vanadia catalyst produces the highest N_2 signal and hence has the highest activity, while wet sulfated 5% vanadia catalyst has the lowest activity. This ordering is inversely related to the observed extent of sulfation and acidity.

These results seem at first glance contrary to expectation, i.e., that the wet-sulfated vanadia catalyst exhibits the lowest activity but would be expected to have the highest surface acidity and hence, highest activity. One explanation is that the NH_3 + NO reaction prefers acid sites of intermediate strength. Therefore, 24-hour sulfation may increase the surface acidity above this intermediate value, thus decreasing catalyst activity. Further acidity studies are expected to supply more information for this study.

XPS analyses

XPS analyses of VTHA, VTOA, VTHB, VTOB, and VTOC indicated zero sulfur content for sulfated catalysts that had been exposed to NH_3. To confirm this result, replicate wet sulfation tests of 5% vanadia catalyst were performed, one with NH_3 adsorption (VTHC), and one without (VTHD). Consistent with the previous results, sulfur disappeared from the sulfated vanadia catalyst upon ammonia exposure and remained on the sulfated vanadia catalyst without ammonia exposure. Those results are summarized in Table 2.

Table 2. XPS analysis results.

	VTHA	VTOA	VTHC	VTHB	VTOB	VTOC	VTHD
	Atom%						
C 1s	11.038	12.446	15.189	12.591	14.756	21.191	15.908
O 1s	63.232	63.01	60.827	62.937	60.995	56.617	60.69
Ti 2p	20.461	20.53	19.219	20.646	20.098	18.272	19.213
V 2p3	3.396	3.863	3.997	3.825	4.152	3.92	4.189
S	1.873	0.151	0.769	0	0	0	0
	with NH_3 adsorption at 380 °C			without NH_3 adsorption at 380 °C			

Disappearance of the sulfate peak was also observed in IR spectra after NH_3 adsorption on sulfated samples. This indicates that ammonia adsorption on a previously sulfated catalyst at 380 °C removes surface sulfate species.

The surface vanadia content is consistent with former results, confirming that the previous analysis of surface composition was valid. Verifying previous results was one of the principal reasons for conducting the experiments reported in this section.

CCS Overview

The catalyst characterization system (CCS) provides capabilities for long-term catalyst exposure tests required for ascertaining deactivation rates and mechanisms and a characterization facility for samples from the slipstream reactor to determine changes in reactivity and responses to well-controlled environments. This system simulates industrial flows by providing a test gas with the following nominal composition: NO, 0.1%; NH_3, 0.1%; SO_2, 0.1%; O_2, 2%; H_2O, 10%; and He, 87.7%. Both custom and commercial catalysts are tested as fresh samples and tested after a variety of laboratory and field exposures under steady conditions.

The CCS quantitatively determines deactivation mechanisms by measuring specific, intrinsic catalyst reactivity of custom (laboratory) and commercial catalysts under a variety of conditions. These catalysts are impregnated with a variety of contaminants, including Ca, Na, and K. In addition, the CCS characterizes samples of catalyst from slipstream field tests to determine similar data and changes in characteristics with exposure. Advanced surface and composition analyses are used to determine composition, pore size distribution, surface area, and surface properties (acidity, extent of sulfation, etc.).

CCS reactor

Consistency between reactors for feed concentration

Tests were run to determine the consistency of concentrations fed to each reactor. Figure 24 shows the variation between the reactors whose feed concentrations were set to 800 ppm. The variation between reactors comes from inconsistencies in mass flow controller flow rates. Subsequent careful mass flow controller calibration reduced variations in concentrations of the reactors to less than 30 ppm for NO, NH_3, and SO_2. This observed variation does not appear to have significant effect on the observed catalyst conversion, as described below.

Note that in Figure 24, the NH_3 concentration is significantly lower than its set point. The reason for this is currently unknown, although it is not a significant concern since the NH_3 concentration can be increased with the reactor control software.

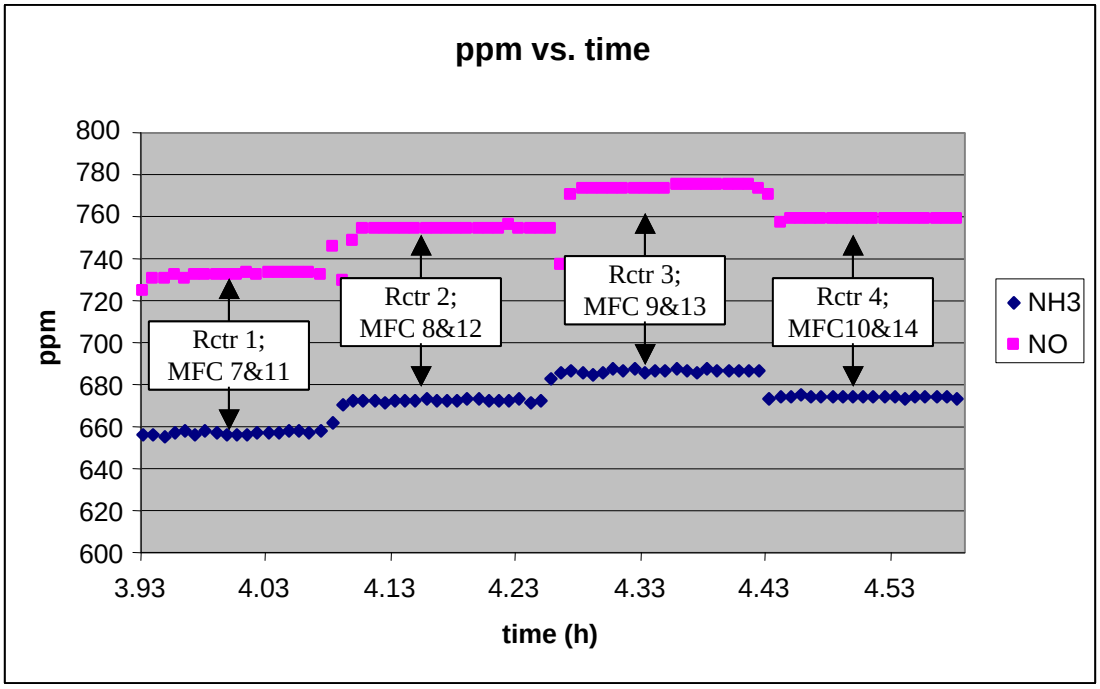

Figure 24. Time-series plot of four empty reactor tubes showing variability of NH_3, NO concentration.

VBA Code written to clean up data

The computer system records data as an ASCII text (.txt) file that is easily read into an Excel worksheet. However, concentration rather than conversion data are recorded, allowing more versatility in data manipulation. The file can easily contain thousands of rows of data, becoming quite large and difficult to manipulate.

An internally written VBA (Visual Basic for Applications) code scans a large data set for groups of concentrations that are associated with either the reactor feed or product (since multiple samples of the feed and product are averaged and recorded over reasonable time intervals) and thus characterizes those concentrations with an average and a standard deviation, greatly reducing the amount of stored data. The groups are clearly labeled so that consecutive measurements of reactor feed and product may easily be compared to calculate conversion data over time, as shown in Equation 1.

$$X_A = 1 - \frac{ppm_{A,out}}{ppm_{A,in}} \qquad (1)$$

Here, X_A is conversion of species A, and $ppm_{A,out}$ and $ppm_{A,in}$ are, respectively, the concentration of A exiting and entering (being fed to) the catalyst. This code was used to find the conversion data that is shown in the following section.

Preliminary Data on Powdered BYU Catalyst

The computer code described previously computed conversion data for preliminary runs on the powdered catalyst prepared at BYU. Data taken under three experimental conditions appear below for each catalyst: 1) isothermal, steady flow; 2) isothermal, increasing flow; and 3) increasing temperature, steady flow. Each test used nominally 200 mg of powdered catalyst packed in a ~0.3 inch ID stainless steel tube with Pyrex wool holding the catalyst plug stationary. Approximately 2% O_2 and 800 ppm each NO and NH_3 entered the reactors (no water or SO_2 were introduced in these preliminary tests). The specifics of each test are discussed below and some conclusions are given.

Isothermal, steady flow rate tests

Figure 25 shows conversion data for the reactors (R1-R4) containing the same amount of the same catalyst (BYU; 200 mg; 220 sccm; 250 °C). R1, R2, and R4 show similar conversion histories, while R3 shows higher conversion. To see whether this was due to the catalyst packing or to mass flow controller inconsistencies, the tubes containing R1 and R2 were swapped, as well as R3 and R4.

After swapping the tubes, similar trends appear in R1, R2, and *R3* (Figure 26 — note that the reactor order is swapped relative to Figure 25). However, R4 conversion is lowest of all. This phenomenon is thought to be due to channeling in the catalyst (when switching the tubes, a thermocouple may have breached the Pyrex wool, forming a channel), although effects of temperature and mass flow controller performance are also suspect.

All reactors report conversions within ±10% and in both sets of experiments three of the four reactors report conversions within ±2%. In these experiments, reactivities of all catalysts should be identical, but in general differences among the reactors such as those illustrated here are indistinguishable from reactivity differences. Therefore, high levels of reproducibility must be consistently achieved to avoid falsely interpreting experimental variation as changes in catalyst activity.

Isothermal, increasing flow rate

Figure 27 shows the effects of increasing flow rate from about 40 to 290 sccm over the catalysts. R1 and R2 operated at 270 °C, while R3 and R4 operated at 241 °C. This temperature difference causes higher conversions in R1 and R2 at the same gas flow rates compared to R3 and R4, as expected.

Same flow rate, increasing temperature

Conversion data vs. temperature for R1-R4 appear in Figure 28. The flow rate was around 220 sccm—about 75% of maximum MFC flow.

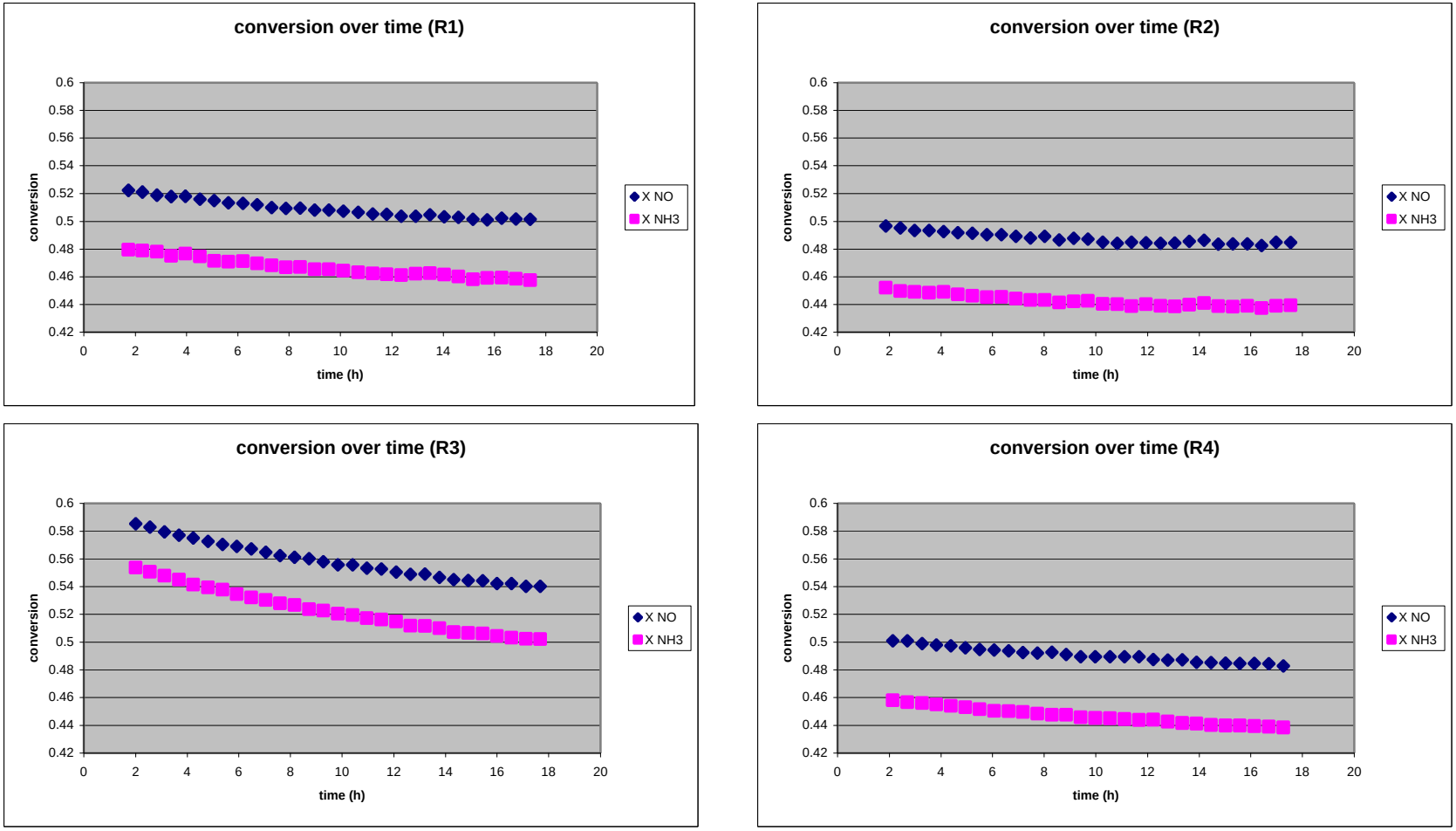

Figure 25. Conversion data for 4 samples of same BYU catalyst run simultaneously.

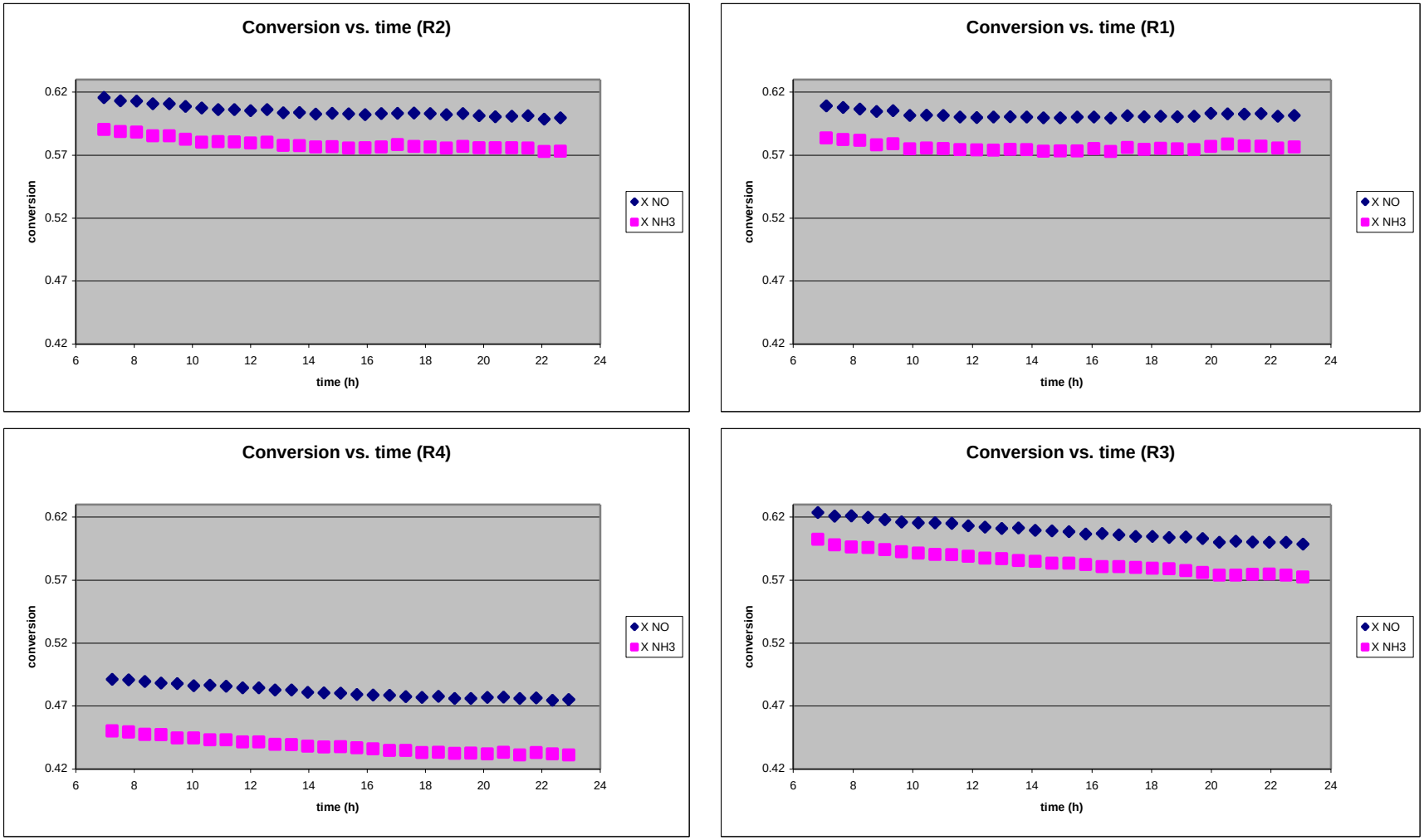

Figure 26. Conversion data after switching R1 and R2, and R3 and R4.

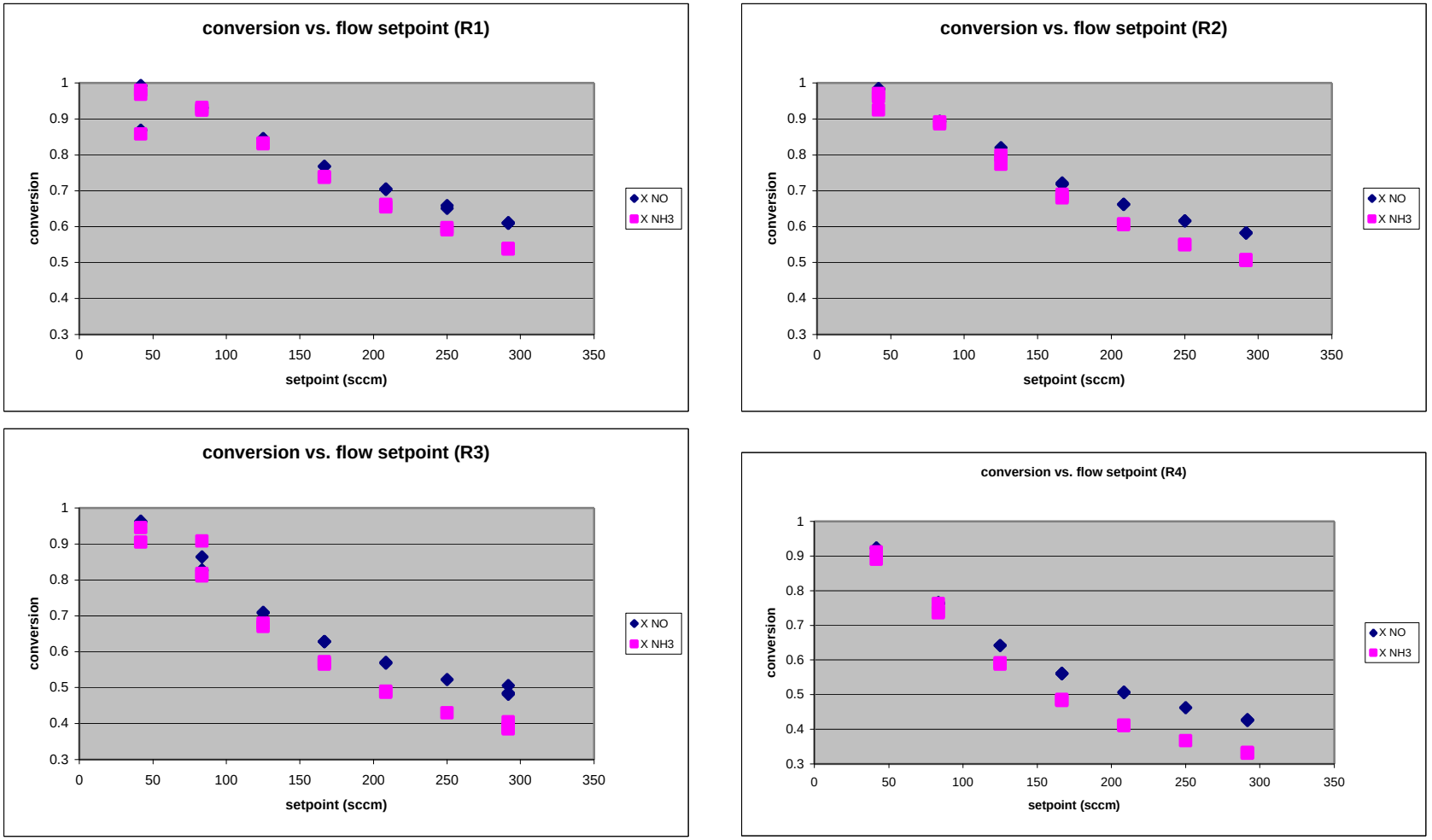

Figure 27. Plots showing decreasing conversion associated with increasing flow rate (space velocity).

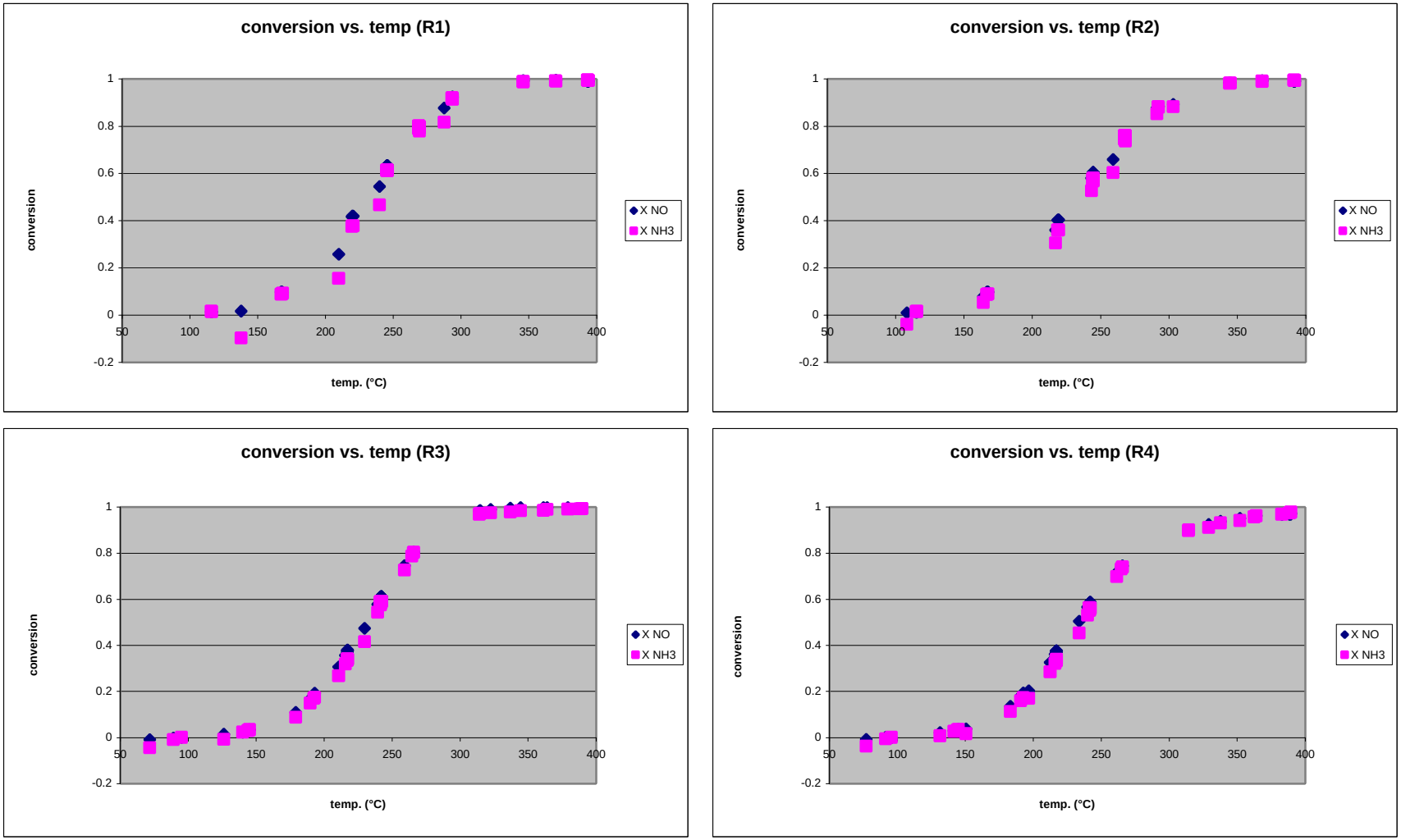

Figure 28. Conversion data as a function of temperature for 4 samples of BYU catalyst.

Conclusions from preliminary BYU catalyst tests.

The tests described above provide some important information regarding the BYU catalyst. First, the catalyst appears to be very active, and it has been speculated by Dr. Calvin Bartholomew that this observed activity is even greater than the commercial catalysts.1 Perhaps, addition of H_2O vapor will lower its activity. Second, to study the catalyst under differential conditions (where conversion is less than 20%), it is necessary to do one or more of the following:

1. Increase the gas flow rate capability of the mass flow controllers to achieve higher flow rates (space velocities) over the catalyst.
2. Reduce the catalyst temperature below the conditions used in an industrial setting (in this case, < 200°C).
3. Reduce the amount of catalyst loaded in the reactor tube.

Each option has its own disadvantage. Option 1 requires modifications and further calibrations on mass flow controllers. The ultimate mass flow controller flow rate can only be extended so far, and the process of extension may exacerbate MFC inaccuracies due to low flow rates and to nonlinearity.

Option 2 is the easiest to do, yet it is perhaps the worst in terms of the effects it may have on the reaction: the activation energies of the elementary steps are strongly dependent on temperature, and the mechanism may be altered if conversion is measured at a lower temperature.2

Option 3 is difficult because further reductions in the amount of catalyst utilized result in a shallow, packed bed that is susceptible to channeling. One option is to reduce the inner diameter of the catalyst zone, which will allow for the same packed *length* with a reduced packed *diameter* and hence, reduced amount of catalyst. A method of doing this is currently under consideration and is illustrated in Figure 29. Here, instead of utilizing an extruded, seamless tube to contain the catalyst, 3/8” OD 316 stainless steel stock will be bored through lengthwise. At some point near the middle of the tubing, the bore diameter will be reduced. The catalyst powder will be placed here. A fritted disc will support the powder and ensure that it remains flat at the bottom, while the top will be secured by Pyrex wool. The fritted disc will be held in place by Pyrex wool also. If the bore method does not work, a small section of reduced-diameter tube can be welded between two segments of 3/8” OD tubing to form the same finished item. Option 3 will be explored first, followed by other measures as necessary.

1 This greater activity may come at the cost of SO_2 oxidation or oxidation of NO to NO_2. Future tests will reveal whether this is true.

2 Dr. Umit S. Ozkan, who has done extensive research in catalysis, suggested that the temperature not be altered from what it is under normal reaction conditions for the reason given here.

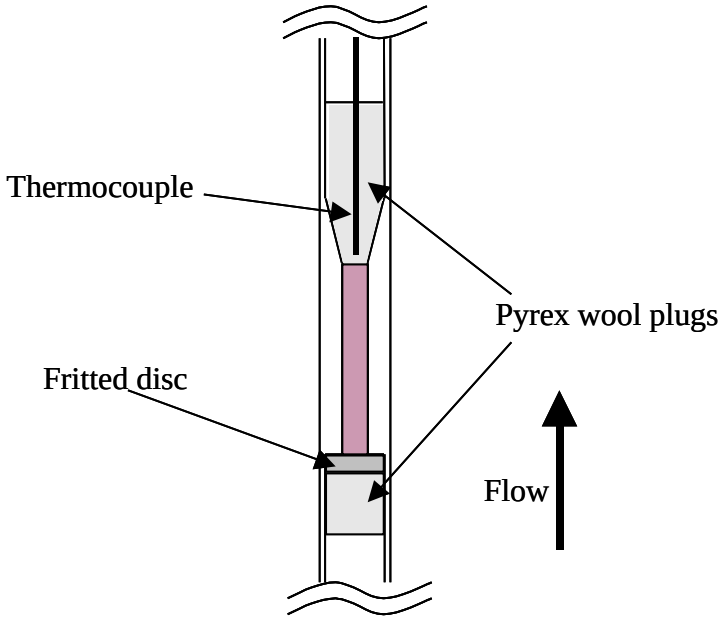

Figure 29. Schematic of new reactor tube design for testing smaller amounts of catalyst.

This section includes data from all four reactors with the same amount of catalyst at nearly identical conditions (i.e. the same temperature, pressure, reactant inlet concentrations within error limits determined by instrumental precision). It is obvious that there are discrepancies between conversion data for different reactors, especially in Figure 25 and Figure 26. It is important that any measured differences among catalysts be due to differences in the catalysts' activities rather than the equipment. Consequently, multiple tests on the same catalyst in different reactors will likely be run so that there are several data points with which statistical tools can be used to compare conversion data.

Analyzer pressure correction

The previous quarterly report contained a discussion of the problems of NH_3/SO_2 analyzer pressure dependence. A more simplified and fundamentally accurate correction method has been applied and is displayed in Equation 2. Here, ppm_{act}, ppm_{obs}, P_{cal}, and P_{inlet} are actual concentration, observed concentration, calibration pressure, and analyzer inlet pressure, respectively.

$$ppm_{act} = ppm_{obs} \cdot \frac{P_{cal}}{P_{inlet}} \qquad (2)$$

Analysis of tubing deposits

The previous report contained some information regarding the deposition of a precipitate inside the tubing where SO_2, NH_3, and NO gases merged. This precipitate was examined with several techniques, including chemical tests, XRD, and HPLC of the dissolved salt. To the best of our knowledge, it is comprised of a mixture of ammonium sulfates and ammonium sulfites, with no nitrate constituent. The compound, weighed before running the HPLC, was estimated to contain ~23 wt% elemental sulfur.3 Also, the HPLC showed two bands in the sulfate region, indicating

3 wt% sulfur in various ammonium sulfate/sulfite compounds ranges from 24-28 wt%

the precipitate in our tubing consists of SO_3^{2-} and SO_4^{2-} species. Oxidation with H_2O_2 solution resulted in one peak (SO_4^{2-}).

The mechanism of ammonium sulfate/sulfite formation is not yet understood, but it is thought that this problem will exist as long as there is SO_2 in the system at virtually any concentration and *especially* in the presence of O_2 or H_2O vapor.4 We will attempt to fix/reduce the ammonium sulfate salt deposits by diluting the upstream SO_2 concentration down from 3%.

Slipstream Reactor Catalysts

Samples of exposed catalysts from the slipstream reactor have been brought to BYU for testing. After initial documentation of the catalysts is performed (e.g. photographs), the catalyst will be tested as described below.

Plans for Testing Monolith Catalysts

Analyses have been performed to determine the feasibility of testing a full-length piece of exposed monolith or plate catalysts from the slipstream reactor. Given budget and time constraints, at this time it will not be feasible to test either full monolith pieces or smaller portions of them. Fortunately, the current reactor setup at BYU will allow for testing of powdered samples, which may be prepared easily by crushing up portions of a commercial plate or monolith.

Although the details are still being planned by Mr. Aaron Nackos for his Master's project, current plans are to first cut the monoliths and plates in half lengthwise (along the z-axis in Figure 30). One half will be preserved so as to have an intact piece for future analysis when a larger, more elaborate reactor system might be built. The other half will be further cut up and various portions crushed up along the length to examine the poisoning profile along the axial direction of the monolith (Figure 31).

Because a poisoning profile should exist both in the axial (lengthwise, or z-direction in Figure 30) and in the horizontal/vertical directions (i.e. profile through the walls of the catalyst, or x-y directions in Figure 30), the catalyst wall surface *and* the interior portions will be analyzed separately to determine intrinsic activity as well as other properties (see Figure 32). Techniques such as microprobe and XPS will also be considered as means to examine the cross-section of a monolith wall, which will not require that the surface be removed.

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4 Dr. Caili Su, a recent visitor to BYU from Japan, experienced the same ammonium sulfate/sulfite salt formation on the catalyst and inside the tubing in her studies of low-temperatures SCR. The conditions in her study varied, but were nominally ~100 °C, 800 ppm SO_2, 250 ppm NO, 500 ppm NH_3. Dr. Su said this deposition was the reason for catalyst deactivation and that it occurred after only a few hours. She also mentioned that it was necessary to replace mass flow controllers 3 times because of fouling in tubes, as well as wash the tubes out with water to purge them of salt buildup. [See Notoya, F., C. L. Su, et al. (2001). "Effect of SO2 on the low-temperature selective catalytic reduction of nitric oxide with ammonia over TiO2, ZrO2, and Al2O3." Industrial & Engineering Chemistry Research 40(17): 3732-3739.]

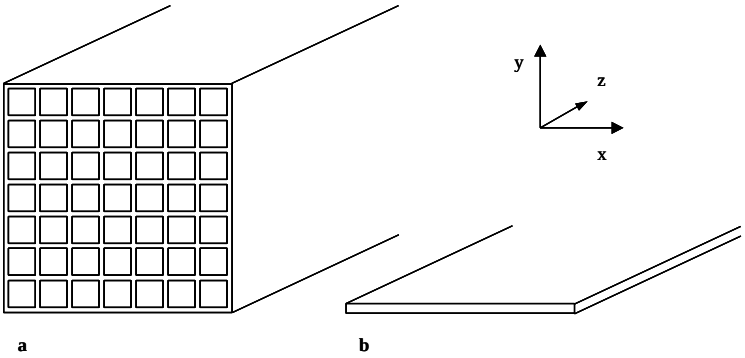

Figure 30. Schematic illustrating a) monolith and b) plate geometries.

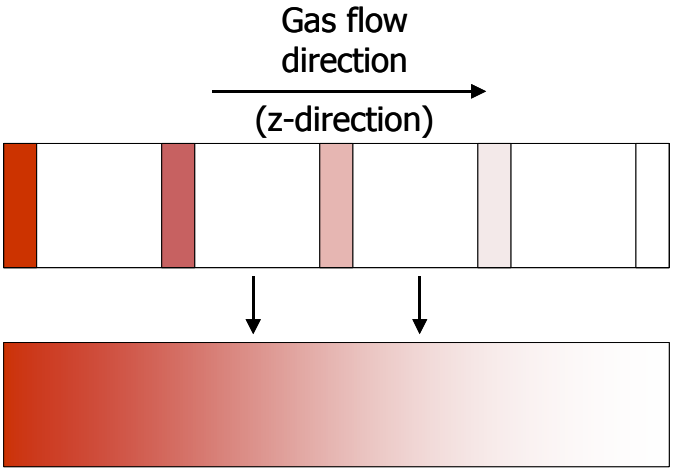

Figure 31. Schematic representing expected poisoning trend in axial direction along monoliths/plates. Darker areas are more poisoned than lighter areas.

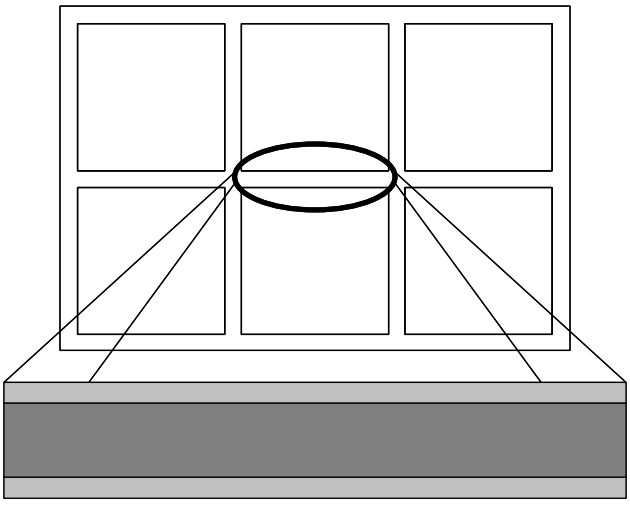

Figure 32. Properties of scrapings of surface of monolith channels or plate surface/interior (light gray, top and bottom) will be compared with bulk catalyst (dark gray, center).

Task 4.2 - Evaluation of Commercial SCR Catalysts for Power Plant Conditions

In accordance with the objectives of this task, the slipstream reactor was operated at AEP's Rockport plant in this quarter and a significant amount of hours of catalyst exposure to the flue gas were accumulated. Figure 33 shows the build up of reactor operating time accrued monthly. In this quarter, the catalysts were exposed to the dusty flue gas for 1695 hours. Thus the cumulative catalyst exposure to flue gas rose from 980 hours last quarter to 2677 hours in this quarter.

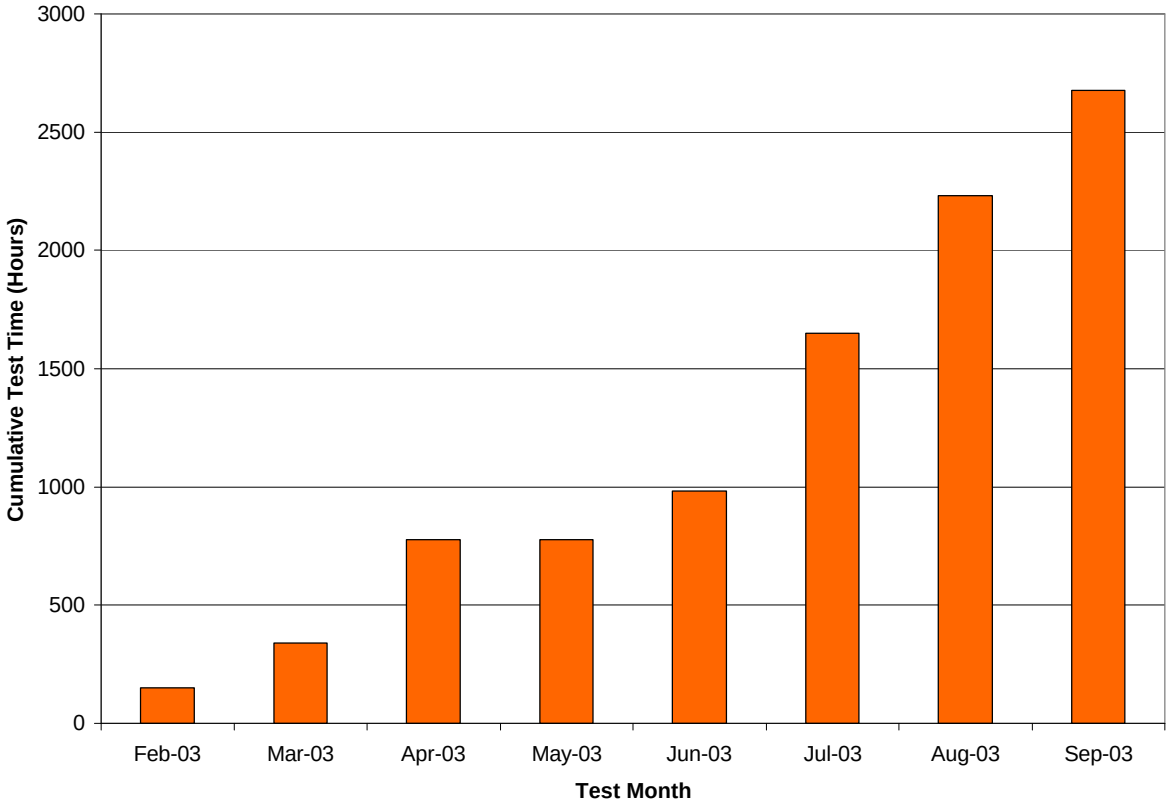

Figure 33. Monthly cumulative catalyst exposure time to dusty flue gas.

Catalyst Activity

The deactivation of commercial SCR catalysts exposed to a flue gas is measured in two ways: (1) by direct measurement of the NO_x composition of the flue gas before and after it flows through a catalyst in the slipstream reactor in the presence of ammonia; and (2) by laboratory evaluation of the catalysts after periodical removal from the slipstream reactor. Figure 34 is a snapshot of catalyst activity obtained from NO_x measurements on August 24, 2003 for all the six catalysts in the slipstream reactor. Figure 35 is a comparison of average catalyst activity from NO_x measurements taken last quarter on April 4, 2003 and this quarter on August 24, 2003. The figure shows a general decline in catalyst activity over the test period.

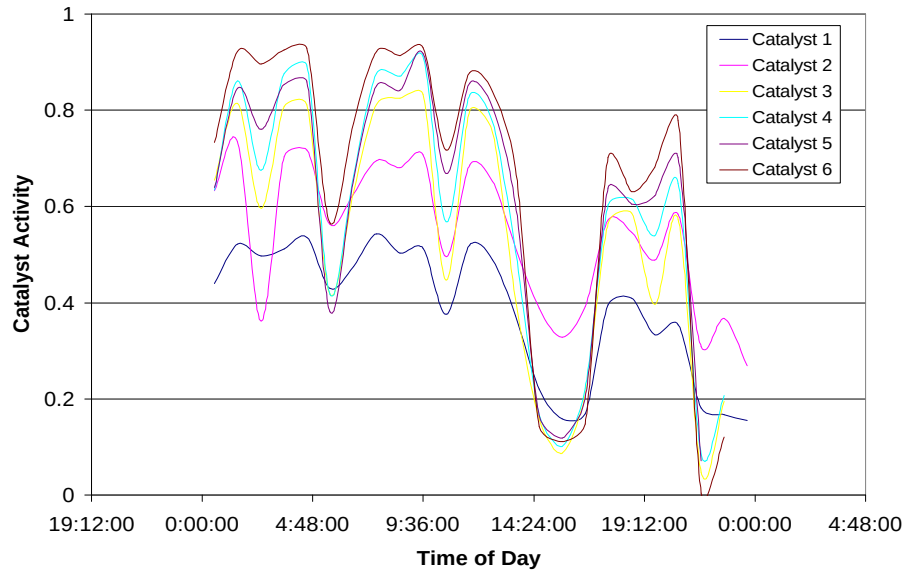

Figure 34. Catalyst activity measurement over a period of 24 hours.

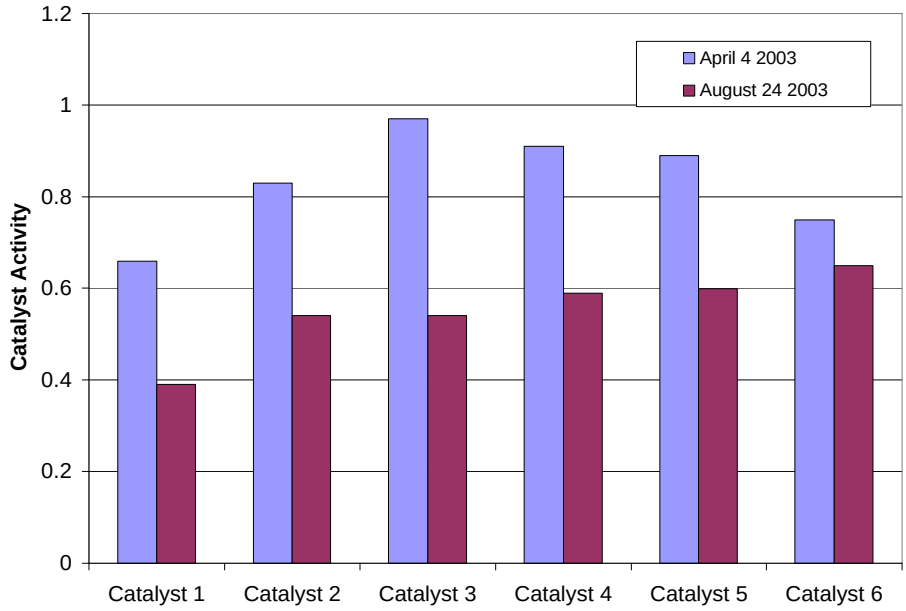

Figure 35. Comparison of catalyst activities measured in April 4, 2003 and August 24, 2003.

In this quarter, catalyst samples were removed from the slipstream reactor for laboratory testing. The samples are currently being analyzed and results will be reported in due course.

Problems in the Reporting Period

Sampling Problems

Sampling problems frequently made NO_x and O_2 measurements unavailable. The problem has been mostly due to plugging of either the sample filters or cementing of ash in the sample line at the entrance to the sample thermo-electric coolers. In this quarter, it was further found that about 50% of the small Teflon connector lines in the hotbox were plugged with ash. These were cleaned and the operating temperature of the hotbox was raised to avoid moisture condensation, which assists cementing of the ash. During mercury oxidation tests in the slipstream reactor, it was observed that one of the dual sampling pumps stopped periodically. Further examination revealed that this problem was caused by the sample gas leaving the coolers being hotter than 10°C, a value hardwired in the SEQUENCER unit. This and other sampling problems are currently being addressed.

Ammonia Venting

In July a team of personnel from REI, AEP and Tanner Industries examined the ammonia venting problem in detail. The team came to a conclusion that the problem was too much pressure in the manifold probably caused by ammonia back-charging. To solve this problem it was suggested to do the following:

(1) run a single cylinder instead of two;
(2) have two regulators in series about 6 feet apart: first regulator steps down the pressure from about 200 psi to 125 psi and the second regulator steps down the pressure from 125 psi to 70 psi; and
(3) shut-off the cylinder when not in use for extended periods of time.

A new ammonia manifold was built based on these recommendations and the ammonia system became operational again since August.

Outage

Testing has been stopped since September 19, 2003 due to an outage that will last until November 2003.

Results and Discussion

The existing corrosion system was configured for a single corrosion probe. In order to build a multi-probe system, additional probes have been fabricated, noise modules and all electronics have been purchased and the data collection software (LabView) has been modified to accept inputs from multiple probes. Existing software and electronics have been modified to add the ability to collect, process and store input signals from sensor elements in six corrosion probes. Monthly project meetings have been held on the corrosion probe task. Two plant visits were made to prepare for field testing, and shakedown tests for the probes were conducted at the University of Utah's L1500 furnace. Corrosion probes will be installed at the Gavin Plant site in the next quarter.

The last quarterly report included results for repeat sulfation treatments of 5 wt% V_2O_5/TiO_2 under both dry and wet conditions performed at BYU in the ISSR; unusually large sulfate IR bands were observed for both dry and wet sulfated vanadia catalysts. Since that time, the outlet of the FTIR reactor was discovered to be plugged with catalyst powder that impeded gas flow. Indeed, the powder blocking the outlet was observed to have the same brownish color as that of the catalyst, while ammonia sulfate is known to be white. Consequently, two more sulfation tests with unobstructed outlets were made to verify that the surface vanadia content would be reasonable and consistent with previous results (3 atom % on surface). In addition, NH_3, and NO adsorption behaviors, both individually and in combination, were investigated by both FTIR and MS analysis of three samples: wet sulfated, dry sulfated, and fresh 5% V_2O_5/TiO_2. XPS analysis was performed to determine surface element atom % of each sample.

Tests in the CCS examined how consistent the reactors are in their conversion with the same amount of the same catalyst (BYU). Efforts to calibrate mass flow controllers have improved the consistency of reactor concentrations. A VBA code was written to clean up and summarize data recorded from the CCS reactor system. Conversion data have been computed for the BYU catalyst and insights have been gained from the results: less catalyst must be used to obtain lower conversions, and better catalyst packing techniques should improve consistency between reactors. The true effect of analyzer inlet pressure on analyzer readout has been accounted for. Deposits on tubing that feeds the reactor have been determined to be ammonium sulfates/sulfites. Plans are being detailed to test monolith and plate catalysts. The catalysts will be cut such that a lengthwise piece is saved for future tests, while the remainder is cut up into smaller segments, each of which will be tested and characterized individually to form a picture of the poisoning/activity profile along the length of the catalyst.

In this quarter, catalysts in the slipstream reactor at AEP's Rockport plant were exposed to the dusty flue gas for 1695 hours. Thus the cumulative catalyst exposure to flue gas rose from 980 hours last quarter to 2677 hours in this quarter. Loss of catalyst activity was noted between April (when the catalysts were fresh) and August.

The Rockport plant is currently in an outage that will last until November. The slipstream reactor is not operating during the outage.

Conclusions

Good progress has been made on several fronts during the last three months. In particular:

- Plant visits were made to Gavin to prepare for field tests of the corrosion probe and to discuss with plant personnel tasks to complete before arrival of equipment. Shakedown testing of one of the corrosion probes was completed at the University of Utah.

- NH_3, and NO adsorption behaviors, both individually and in combination, were investigated at BYU by both FTIR and MS. The NH_3+NO reaction occurs on the catalyst surface *in the absence of* O_2. Unsulfated 5% vanadia catalyst produces the highest N_2 signal and hence has the highest activity, while wet sulfated 5% vanadia catalyst has the lowest activity.

- XPS analysis was performed to determine surface element atom percentage of each sample. Disappearance of the sulfate peak was observed after NH_3 adsorption on sulfated samples. This indicates that ammonia adsorption on a previously sulfated catalyst at 380 °C removes surface sulfate species. The surface vanadia content is consistent with former results, confirming that the previous analysis of surface composition was valid.

- Tests in the CCS examined how consistent the reactors are in their conversion with the same amount of the same catalyst (BYU). Conversion data have been computed for the BYU catalyst and insights have been gained from the results.

- The slipstream reactor continued to operate at AEP's Rockport plant. At the end of the quarter, the catalysts had been exposed to flue gas for about 2677 hours. Data collected on catalyst activity showed a decrease in activity from April to August. The first catalyst samples were pulled at the end of the quarter and sent to BYU.

Plans for Next Quarter

Corrosion probe activity for the next quarter will focus on the following:

- Completion of the probe shakedown tests
- Completion of assembly of all probes
- Assembling the control boxes and testing the control software with six probes connected
- Making preparations for the Gavin corrosion tests
- Shipping the equipment to Gavin
- Installation of equipment at Gavin and commencement of corrosion test

SCR slipstream activity for the next quarter will focus on the following:

- Preparing a manuscript that will address procedures for monolith/plate analysis as well as effects of catalyst poisons. BYU will begin to prepare the commercial catalysts for analysis, perform characterization tests, and continue to prepare and fine-tune the CCS reactor system for accurately testing catalyst samples.

- Rockport Unit 1 will be shut down through late November to install low NO_x burners. After the plant is back on-line, the SCR reactor will be started up again.